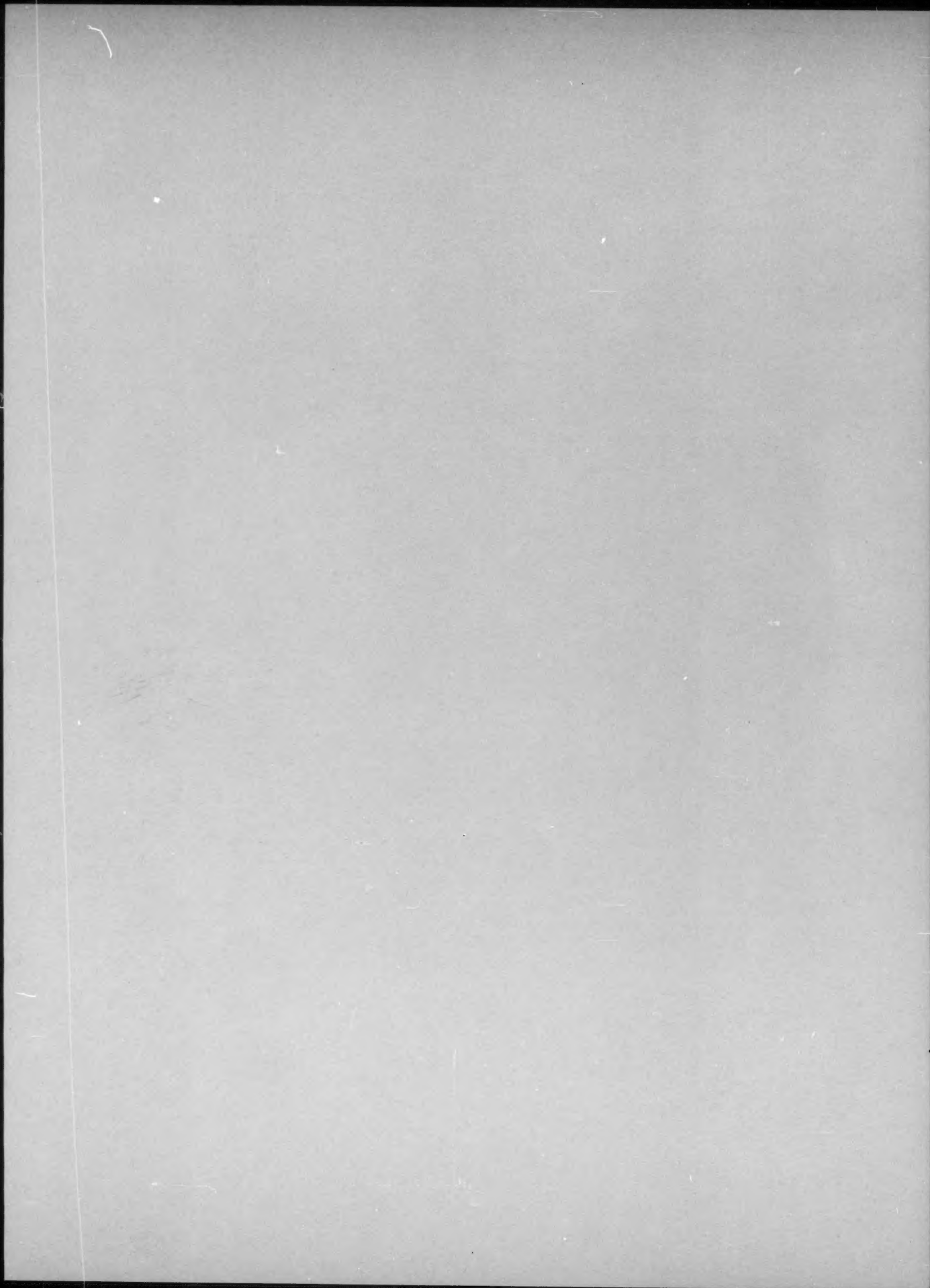


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BEHAVIOR AND PROPERTIES OF THE ALKALI METALS IN SILICATE GLASSES¹⁾

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According to contemporary X-ray information, neither free alkali metal oxides, Me_2O , nor definite structural groups containing two Me^+ ions and one O^{2-} ion are present in glasses. In general, discrete molecules are absent from the structure of glasses. However, admitting that glasses are ionic systems in which there are no free oxide molecules, we still consider it very convenient to express their composition in terms of oxides and to study the partial properties of these oxides as though they were components. This question has already been discussed in detail in an earlier paper [1]. We there described a method of calculating partial properties of the components \bar{g}_i , and examined the results obtained for the partial properties of silica (\bar{N}_{SiO_2} , \bar{V}_{SiO_2} , \bar{D}_{SiO_2} , $\bar{\alpha}_{\text{SiO}_2}$). We put forward empirical Equations (6), (7), (8) on the basis of this data, these equations permitted the approximate calculation of the partial properties of silica in glasses as a function of their SiO_2 content: this involved the assumption that these equations are correct for all silicate glasses. This assumption is close to the truth for properties such as \bar{N}_{SiO_2} , \bar{V}_{SiO_2} , and \bar{D}_{SiO_2} , and it appears to be valid to assume it to be true for $\bar{\alpha}_{\text{SiO}_2}$ at least for practical purposes.

We calculated the values of the partial properties of the alkali oxides $\bar{g}_{\text{Me}_2\text{O}}$ by difference, with the aid of Equation (4), preferably from binary systems using known values of \bar{g}_{SiO_2} (i.e. more correctly, those found from Equations 6-8)²⁾. In this way we found partial properties which are not the strict thermodynamic ones, but are approximate or averaged partial values $\bar{g}_{\text{Me}_2\text{O}}$.

However, the great diversity in composition of glass completely justifies such an approach to the solution of the problem.

The results of the calculations are presented graphically in Figs. 1, 2, and 3, to which are appended the sources from which the experimental material for the calculations have been drawn. We synthesized a number of the glasses. Along the ordinate are plotted the numerical values of the various partial properties, characteristic of the oxides in the glasses, and along the abscissa are plotted the oxide contents in the glasses, in percentages.

¹⁾ Communication II dealing with the investigation of the relation between the properties and composition of glasses.

²⁾ For the calculation of the values of $\bar{g}_{\text{Li}_2\text{O}}$ we used the results of the investigation not only of binary systems, but also of more complex ones. In the latter case these values were calculated after the average \bar{g}_i values were found for all the other oxides entering into the composition of the system under examination. (These results are to be presented in later papers).

From Fig. 1 it can be seen that each of the values \bar{g}_{Li_2O} , (apart from \bar{a}_{Li_2O}), is expressed in terms of two average numerical values. The dotted lines relate to points found for the binary system Li_2O-SiO_2 . The solid lines relate to points for three-component or more complicated systems.

We group the points for the average partial properties \bar{g}_{Na_2O} and \bar{g}_{K_2O} likewise into two lines (Figs. 2 and 3) although the difference between them is not great. Points are shown only for binary systems (dotted lines). The solid lines, representing the partial properties of the oxides K_2O and Na_2O in three-component and more complicated systems, are drawn without indicating the points.

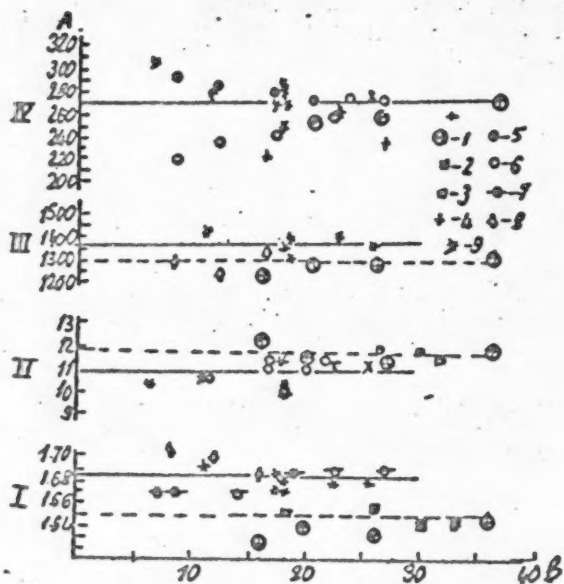


Fig. 1. Approximate values of the partial properties of lithium oxide in silicate glasses.

A: I - \bar{N}_{Li_2O} , II - \bar{V}_{Li_2O} , III - $\bar{D}_{Li_2O} \cdot 10^5$, IV - $\bar{a}_{Li_2O} \cdot 10^7$; B - Li_2O content (in %).

Li_2O-SiO_2 : 1 - Appen [1], 2 - Kratsek [4]; 3 - Hubbard [8]; 4 - Dietzel and Sheybany [9]; $Li_2O-Na_2O-CaO-SiO_2$; 5 - Waterton and Turner [10]; $Li_2O-K_2O-CaO-SiO_2$; 6 - Waterton and Turner [10]; $Li_2O-Al_2O_3-SiO_2$; 7 - Hatch, [6]; $Li_2O-B_2O_3-SiO_2$; 8 - Hamilton et al [7]; $Li_2O-MeO-SiO_2$; 9 - Appen.

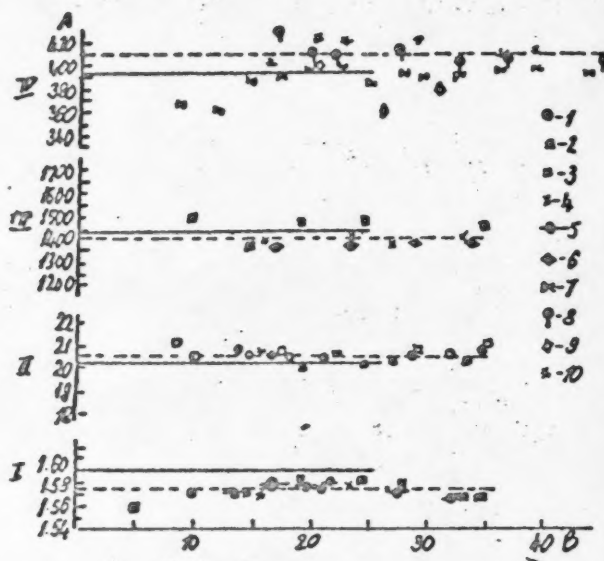


Fig. 2. Approximate values of the partial properties of sodium oxide in silicate glasses.

A: I - \bar{N}_{Na_2O} , II - \bar{V}_{Na_2O} , III - $\bar{D}_{Na_2O} \cdot 10^5$, IV - $\bar{a}_{Na_2O} \cdot 10^7$; B -

Na_2O content (in %). System Na_2O-SiO_2 : 1 - Young et al [5]; 2 - Morey and Mervin [4]; 3 - Winks and Turner [4]; 4 - Krakau [3]; 5 - Feik and Fink [4]; 6 - Peddle [4]; 7 - Turner and Winks [4]; 8 - Schmidt, Finn and Young [4]; 9 - Dietzel and Sheybany [9]; 10 - Appen [1].

The solid lines on the figures correspond to the values of \bar{g}_{Me_2O} at which each of the values \bar{g}_{MeO} for the alkaline earth oxides can, in the majority of cases, be expressed satisfactorily by one and the same average constant figure, more or less independent of the nature of the alkali oxide present.

Consequently, the question arises as to whether such division of the partial

properties of the alkali oxides has a real basis, or whether it is only based on practical convenience.

The following facts should serve to answer this question.

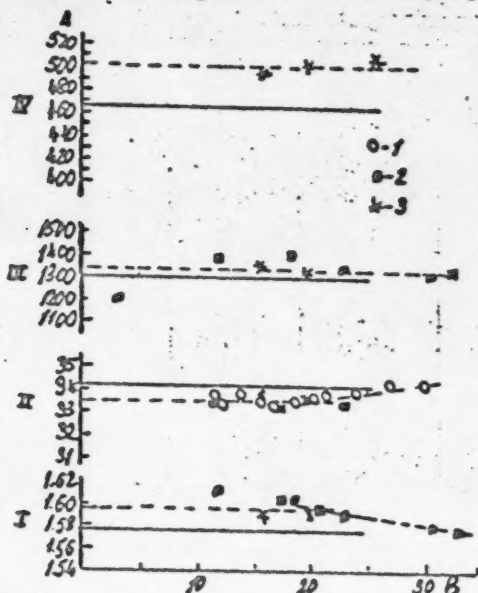


Fig. 3. Approximate values of the partial properties of potassium oxide in silicate glasses.

A: I - \bar{V}_{K_2O} , II - \bar{V}_{K_2O} , III - $\bar{D}_{K_2O} \cdot 10^5$, IV - $\bar{\alpha}_{K_2O} \cdot 10^5$; B - K_2O content (in %).

System K_2O-SiO_2 : 1- Young et al [5]; 2 - Mervin and Morey [4]; 3- Appen [1].

simplify the observations by saying that the change due to the introduction of the third component is exerted only on the alkali oxide. This is certainly an approximation, but it represents the actual state of affairs to a large extent.

The ability of alkali oxides to change their properties on transferring from binary to more complex systems can be demonstrated in a much more definite form by many examples relative to the chemical stability and electrical conductivity of glasses.

It is known that the alkali can be extracted from binary silicates by water about ten times as easily as from complex glasses containing the same quantity of alkali, but with one of the oxides of the divalent metals present.

The doubly charged barium and calcium ions, when present in large concentration, can lower the mobility of sodium ions, relative to their mobility in a binary system, by a factor of 100 or more [2]. Thus not only a small but a large change of some partial properties of alkali oxides, on going from a binary to a more complicated system, can be taken as established. The cause of this change has not yet been explained.

Figures 1, 2, and 3, demonstrate that the values of \bar{N}_{Me_2O} , \bar{V}_{Me_2O} , \bar{D}_{Me_2O} , $\bar{\alpha}_{Me_2O}$, characteristic of the properties of the alkali oxides in glass, fall in general on straight lines parallel to the abscissa. Strictly speaking, the

The two-component potash-silica glasses have a higher refractive index n_D than soda glasses of the same molecular composition. The same is true for the density of these glasses, though over a narrower range of composition (0-20 mol % Na_2O). In three-component glasses where the third component is an element of higher valency the relation between these properties is inverted. The refraction index and the density of potash glasses are, as a rule, lower than those of the corresponding soda glasses (Table 1). This rule applies also in the more complicated multi-component glasses.

Thus, the relationship between the properties and composition of complex glasses differs from that in binary systems of the type Me_2O-SiO_2 . Evidently, as a result of the complication in the composition, there is a considerable change in the partial properties of the components in the binary systems. Strictly speaking, there is a change of properties of both the Me_2O and SiO_2 . However, as we have already indicated, the effect on the partial properties of SiO_2 is quite small, and it is possible to

TABLE 1
Comparison of the Properties of Lithium, Potassium
and Sodium Silicate Glasses

Property	Series $\text{Me}_2\text{O} \cdot \text{MeO} \cdot 3.75 \text{ SiO}_2$				
	Me_2O	BeO	MgO	CaO	SrO
Refractive index n_D	Li_2O	1.5341	1.5386	1.5594	1.5625
	$\Delta n_D \cdot 10^4$	+176	+255	+205	+147
	Na_2O	1.5165	1.5131	1.5389	1.5478
	$\Delta n_D \cdot 10^4$	+41	+103	+67	+77
Mean dispersion ($n_F - n_C$) $\cdot 10^5$	K_2O	1.5124	1.5028	1.5322	1.5401
	$\Delta(n_F - n_C) \cdot 10^5$	837	884	943	956
	Na_2O	843	884	946	974
	$\Delta(n_F - n_C) \cdot 10^5$	+30	+48	+31	+43
Density, d	K_2O	813	836	915	931
	Li_2O	2.394	2.455	2.539	2.850
	$\Delta d \cdot 10^3$	-92	-39	-51	-40
	Na_2O	2.486	2.494	2.590	2.890
Average linear co- efficient of ex- pansion $\alpha_{20-400} \cdot 10^7$	$\Delta d \cdot 10^3$	+28	+59	+40	+92
	K_2O	2.458	2.435	2.550	2.798
	Li_2O	74.8	86.5	94.4	101.4
	$\Delta \alpha \cdot 10^7$	-26.3	-16.2	-19.4	-20.6
	Na_2O	101.1	102.7	113.8	122.0
	$\Delta \alpha \cdot 10^7$	-6.1	-4.5	-1.6	-1.3
	K_2O	107.2	107.2	115.4	123.3
	$\text{Na}_2\text{O} + \text{K}_2\text{O}$ (1:1)	111.2	112.5	121.4	128.4

*Note: The average coefficient of linear expansion of the glasses containing PbO was determined over the range 20-350°.

observed scattering of the points, or the tendency which they show to some deviation from the parallel lines, in particular in the system $\text{K}_2\text{O}-\text{SiO}_2$, is to be explained not only in terms of experimental error, but also in terms of some change of the partial properties of the oxides in going from glasses of one composition to another. But the role of the second factor is not large, since the deviation of the points from the straight lines corresponds to a very small change in the properties of the glass. Hence it can be taken that, within the limits of one group of systems (binary or more complex), the properties of the oxides in glasses examined remain comparatively stable within a definite, but wide, field of composition.

The comparative stability of the properties of alkali oxides in complicated glasses is confirmed well by a series of our own experiments. We have shown that if the properties, for example the molar refractive indexes n_D , of three-component glasses of different molar compositions are compared, the figure for potash glass is, as a rule, somewhat smaller than that for soda glass, and the figure for the latter is a great deal less than that for lithia glass; soda glass has the highest dispersion, $n_F - n_C$, that for potash glass being smaller, and that for lithia glass intermediate between them. The density of soda glasses, as a rule is higher than the density of lithia and potash glasses. The coefficient of linear expansion of lithia glasses, in all cases, is considerably less than that

TABLE 1
Comparison of the Properties of Lithium, Potassium
and Sodium Silicate Glasses

Series $\text{Me}_2\text{O} \cdot \text{MeO} \cdot 3.75 \text{ SiO}_2$				Series $0.8 \text{ Me}_2\text{O} \cdot \text{MeO} \cdot 3.2 \text{ SiO}_2$	
BaO	ZnO	CdO	PbO	B ₂ O ₃	TiO ₂
1.5842	1.5544	"Blank"	1.6668	"Blank"	"Blank"
+188	+185	-	+203	-	-
1.5654	1.5359	1.5634	1.6465	1.5193	1.6363
+ 88	+ 70	+ 93	+123	+ 43	+312
1.5566	1.5289	1.5541	1.6342	1.5150	1.6051
1010	979	-	1924	-	-
- 14	- 2	-	- 20	-	-
1024	981	1137	1944	797	1898
+ 39	+ 43	+ 41	+ 74	+ 30	+277
985	938	1096	1870	767	1621
3.130	2.736	-	3.825	-	-
- 14	- 44	-	+ 29	-	-
3.144	2.780	3.070	3.796	2.484	2.678
+ 85	+ 53	+ 80	+141	+ 19	+ 76
3.059	2.727	2.990	3.655	2.465	2.602
106.8	74.6	92.2	91.6*	59.2	-
-22.6	-22.2	-19.6	-29.6	-24.2	-
129.4	96.8	111.8	121.2*	83.4	88.0
- 2.7	-14.3	- 5.6	- 7.0	- 2.9	- 6.3
132.1	111.1	117.4	128.2*	86.3	94.3
135.9	110.5	119.0	123.6	90.0	95.8

Note: The average coefficient of lineary expansion of the glasses containing PbO was determined over the range 20-350°.

of soda glasses, while the difference between these coefficients for soda and potash glasses is small. Potash glasses have only a slightly larger coefficient of linear expansion than soda glasses.

The experimental data is given in Table 1.

From this table it can be seen that the difference between the properties of lithia, soda and potash glasses is usually of the same order and sign. The similarity between these figures would be still better if there were not unavoidable deviations of the actual composition from the synthetic. Only the optical properties of titania glasses are anomalous, and these will be dealt with later.

We have examined above the properties of three-component glasses, containing only one alkali oxide. Those compositions in which both soda and potash are present simultaneously are of great practical importance. The question arises as to whether the properties of these compositions are intermediate between those for the pure soda and pure potash compositions. Experiment shows that this is not always the case. With replacement of one oxide by another, as was found by Peddle [4], a weak maximum is formed on the curve of variation of n_D with composition. We found a similar state of affairs in relation to the coefficient of linear expansion. Soda and potash glasses, from the series indicated in Table 1, were ground up, mixed in the molar ratios of 1:1 and then remelted. It was found that in the majority of cases, such mixed glasses had higher coefficients of

expansion than the original glasses. Concrete cases are given in Table 1. Consequently, the curves of variation of α with gradual replacement of one alkali by another, should pass through maxima.

These facts demonstrate that the earlier noted comparative stability of the partial properties of the Me_2O oxides in glass is of limited significance.

The data examined above relative to the behavior and properties of the alkali metal oxides in silicate glasses are presented in a simple and convenient form in Table 2, where the partial properties of the oxides, $\bar{E}_{\text{Me}_2\text{O}}$ are given as approximate averaged constant values.

TABLE 2

Approximate-average Values of the Partial Properties $\bar{E}_{\text{Me}_2\text{O}}$ of the Alkali Metal Oxides in Silicate Glasses

Oxide	Type of glass	Refractive Index $\bar{n}_{\text{Me}_2\text{O}}$	Molar volume $\bar{V}_{\text{Me}_2\text{O}}$ (cm^3/md)	Mean dispersion $\bar{D}_{\text{Me}_2\text{O}} \cdot 10^5$	Mean linear coefft. of expansion $\bar{\alpha}_{\text{Me}_2\text{O}} \cdot 10^7$	Limits of application. Content of oxides in glass (in mol %)
Li_2O	Complex glass.....	1.695	11.0	1380	270	0 - 30
	System $\text{Li}_2\text{O}-\text{SiO}_2$	1.660	11.9	1300	270	0 - 40
Na_2O	Complex glass.....	1.590	20.2	1420	395	0 - 25
	System $\text{Na}_2\text{O}-\text{SiO}_2$	1.575	20.6	1400	410	0 - 35
K_2O	Complex glass.....	1.575*	34.1*	1300*	465*	0 - 20
	System $\text{K}_2\text{O}-\text{SiO}_2$	1.595	33.5	1320	500	0 - 25

Note: The values of $\bar{E}_{\text{K}_2\text{O}}$ starred (*) indicate the properties of K_2O mainly in the presence of Na_2O . In pure potash glasses the average numerical values of the $\bar{E}_{\text{K}_2\text{O}}$ are somewhat different. For ratios $\text{Me}_m\text{O}_n/\text{K}_2\text{O}$ lying inside the range of compositions for practical glasses, we have:

$$\bar{n}_{\text{K}_2\text{O}} \approx 1.560; \bar{V}_{\text{K}_2\text{O}} \approx 34.5; \bar{D}_{\text{K}_2\text{O}} \cdot 10^5 \approx 1250; \bar{\alpha}_{\text{K}_2\text{O}} \cdot 10^7 \approx 425.$$

The division of the partial properties of $\bar{E}_{\text{Me}_2\text{O}}$ into two groups of constant numerical characteristics should be taken as practically convenient, but theoretically simplified and approximate. When introducing increasing quantities of a third component Me_mO_n (oxides of the 2, 3 and 4-valent elements), the properties of the Me_2O oxide do not change immediately, but gradually, according to a definite law which has still not been studied. Naturally the quantity of the component introduced is of importance: the larger this quantity, compared with the quantity of the Me_2O oxide, the more strongly do the partial properties of Me_2O ($\bar{E}_{\text{Me}_2\text{O}}$) deviate from those for a binary system.

The complexity of the behavior of Na_2O and K_2O , when present together in a glass, has not so far been capable of being given any mathematical form since there has not been sufficient experimental material. In spite of this, by deducing average values for the $\bar{E}_{\text{K}_2\text{O}}$ quantities, we took these peculiarities into consideration. Since in practice pure potash compositions are rarely used, we preferred to obtain the average values of $\bar{E}_{\text{K}_2\text{O}}$ from mixed compositions. The numerical values of $\bar{E}_{\text{K}_2\text{O}}$ in Table 2 reflect the properties of mixed compositions better than those of pure potash glasses. For the latter the average $\bar{E}_{\text{K}_2\text{O}}$ values are indicated in the note at the bottom of Table 2.

The results in Table 2 show that the oxides can be arranged, relative to some of their properties, in an order corresponding to the periodic classification (under molecular volume, coefficient of linear expansion), but if the arrangement is based on the other properties, the order is not the same.

The limits of use of the numerical values of \bar{g}_{Me_2O} cover the whole range of compositions of glasses of practical interest. Only when the quantity of alkali exceeds 20-30% is there a considerable deviation of the actually measured \bar{g}_{Me_2O} values from those given in Table 2, and even then the deviation is regular. For example, the values of \bar{n}_{Me_2O} for all three oxides tend to decrease as the alkali- nity of the glass increases, which would also be expected, at any rate for Li_2O , because the average refractive index of Li_2O in the free state is less than in glass, and consequently the partial \bar{n}_{Li_2O} should tend toward this as a final limit, i.e. to the refractive index of pure Li_2O , which is 1.644. The refractive indices of the other alkali oxides are unfortunately not known but they should be less than the values found for \bar{n}_{Me_2O} .

We carried out a series of experiments, aimed at confirming this independence by getting reliable values for the \bar{g}_{Me_2O} quantities, which are set forth in Table 2 and are fixed by the graphical position of the solid lines in the figures.

For this purpose we compared three-component glasses of the type Me_2O - BaO - SiO_2 , whose composition was changed in such a way that, as the mol fraction of Me_2O in the glass increased, the ratio SiO_2/BaO remained constant at 3.75. The optical properties of the glasses were determined, followed by the density and the coefficient of expansion, and from these measurements the corresponding partial values \bar{g}_{Me_2O} were calculated via the thermodynamic Equation (5a). The results are shown in Table 3.

TABLE 3

Partial values of the Alkali Oxides in Glasses of the Type Me_2O - BaO - SiO_2

Expt. No.	Composition of the glass (in mol fractions)			Composition of the glass				Partial properties of the alkali oxides			
	SiO_2	Me_2O	BaO	n_D	d	$(n_F - n_C) \cdot 10^5$	$\alpha_{20-100} \cdot 10^7$	\bar{n}_{Me_2O}	\bar{v}_{Me_2O}	$\bar{D}_{Me_2O} \cdot 10^7$	$\bar{\alpha}_{Me_2O} \cdot 10^5$
Li_2O											
1	0.7426	0.0594	0.1980	—	3.128	—	80.8	—	9.68	—	302
2	0.7010	0.1120	0.1870	1.5752	3.127	986	93.2	1.704	9.23	1331	289
3	0.6520	0.1740	0.1740	1.5842	3.130	1010	106.8	1.668	13.50	1445	241
4	0.6146	0.2214	0.1640	1.5890	3.098	1035	114.5				
Average value.....								1.686	10.8	1390	275
Na_2O											
1	0.7426	0.0594	0.1980	1.5617	3.130	967	85.7	1.599	18.67	1431	513
2	0.7010	0.1120	0.1870	1.5638	3.138	993	109.7	1.587	19.10	1439	393
3	0.6520	0.1740	0.1740	1.5654	3.144	1024	129.4	1.550	22.82	1390	372
4	0.6146	0.2214	0.1640	1.5645	3.121	1045	143.3				
Average value.....								1.580	20.2	1420	425
K_2O											
1	0.7426	0.0594	0.1980	1.5543	3.082	947	92.9	1.569	32.71	1162	439
2	0.7010	0.1120	0.1870	1.5551	3.068	959	112.3	1.577	31.84	1333	397
3	0.6520	0.1740	0.1740	1.5566	3.059	985	132.1	1.576	34.37	1316	521
4	0.6146	0.2214	0.1640	1.5577	3.036	1004	154.4				
Average value.....								1.574	33.0	1270	450

Some of these partial values \bar{g}_{Me_2O} change appreciably in one direction, but none the less it is possible to average them. The observed differences in the partial values \bar{g}_{Me_2O} correspond only to small deviations in the properties of the glasses from the averaged values.

If it is considered that the accuracy of the determination of the partial values is small, because small errors in the composition of the glass can exert large effects on the $\epsilon_{\text{Me}_2\text{O}}$ values, then the results obtained should be looked on as good confirmation of the correctness of using average partial values for the complex systems.

SUMMARY

1) The refractive index, mean dispersion, density and average coefficient of linear expansion over the range 20-400° have been determined for some series of silicate glasses. The experimental data obtained, in conjunction with that of other investigators, has been used to calculate the values of the partial properties $\epsilon_{\text{Me}_2\text{O}}$ for the oxides of the alkali metals in silicate glasses.

2) It has been shown that the relation between the properties named and the composition of three-component glasses of the type $\text{Me}_2\text{O}-\text{MeO}-\text{SiO}_2$ (or more complicated ones) is essentially different from that between the properties and composition of binary glasses.

3) In order to express this difference in more simple quantitative form, the practical device of replacing the strict thermodynamic partial quantities by approximate and averaged ones has been introduced; these values have been divided into two series: one of the partial properties in binary systems, and the other of the partial properties in three-component and more complicated systems.

4) The possibility of presenting the approximate partial quantities in the form of averaged constant numerical characteristics is conditioned by the fact that the change of the partial properties within the limits of one type of system, binary or more complicated, is small in the majority of cases, and can be neglected so long as the content of Me_2O in the glass does not exceed 20-30 mol %.

5) It has been found that the curves expressing the variation of the coefficient of linear expansion of glasses, when one alkali oxide (Na_2O) is gradually replaced by another (K_2O) should in many cases pass through a pronounced maximum. This demonstrates the fact that the conclusions formulated above, about the relative stability of the partial properties of the Me_2O oxides in glasses, is of limited significance.

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¹⁾See C.B. Translation, p. 1027.

HEAT OF VAPORIZATION OF OXIDES OF NITROGEN FROM NITROSE

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The work which has been done [1, 2] to establish the functional relationship between the equilibrium pressure of nitrogen oxides over nitrose and the factors on which it depends for the systems (H_2SO_4 , H_2O , N_2O_3) and (H_2SO_4 , H_2O , H_2O_3 and HNO_3) also enables a calculation to be made of the heat of vaporization of oxides of nitrogen from nitrose, which is one of the characteristics of these systems from the energetics point of view.

In the present paper the effect of such separate factors on the heat of vaporization of oxides of nitrogen from nitrose is also examined, and the calculated heats of vaporization are compared with those to be found in the literature.

Apart from their theoretical interest, these values have practical importance for the compilation of technological balances for nitrose in sulfuric acid manufacture.

As is known, the heat of vaporization of solutions may be determined by experimental measurement or from data relative to the heat of vaporization of the pure components and the heat of mixing or, finally, from the saturation vapor pressure above the solutions. Masing compared the results of measurement of the heat of vaporization by individual indirect methods [3], and he came to a negative conclusion. Kireev [4], working on the same theme, showed on the contrary that all three methods give comparable results within the limits of error of the assumptions made.

The molar heat of vaporization of liquids may also be determined by using Trouton's rule. Several equations have been proposed for calculating a modernized Trouton's constant, corresponding better with the results of experiments. The most comprehensive thermodynamic equation is that of Kistyakovsky [5]. All these equations, however, apply only to non-polar liquids.

From Herz's results [7], Kireev [6] showed that there is a parallel between the change of the dimensionless parameter L/RT (where L = molar heat of vaporization, R = the universal gas constant, T = absolute temperature) with the temperature for different substances in corresponding states.

This method is convenient for the study and expression of the temperature dependence of the heat of vaporization.¹

Some analogous graphical procedures were proposed by Watson [8].

Hildebrand [9] showed that the molar entropy of vaporization (L/T) is approximately constant for substances having different boiling points at atmospheric pressure, if the molar entropy values are compared at temperatures at which the vapor concentrations of the substances are equal, and if the calculation is restricted to pressures at which the vapors obey the ideal gas law.

We have found, in the literature, references to experimental work on the determination of the heat of absorption of oxides of nitrogen by sulfuric acid - that of Kartashev and Tseitlin [10]. We shall dwell in somewhat more detail on

1) Absence of any figures for the critical constants of N_2O_3 prevents us from pursuing this dependence.

their work.

For experiments carried out in a Dewar vessel, 400-450 ml of acid containing 76.5-80% H_2SO_4 was taken. The temperature of the experiments was 20-25°. The acids were vigorously stirred and oxides of nitrogen passed in. N_2O_3 was produced from sodium nitrite and sulfuric acid. In experiments with NO_2 , the latter was obtained by heating lead nitrate. The gas introduced for absorption was previously dried by passage through a P_2O_5 drying tower. The nitrose formed was analyzed by titration with 1 and 2 N permanganate and also in a nitrometer.

The nitrose formed in experiments with N_2O_3 contained 0.15-1.5% N_2O_3 , and in experiments with NO_2 , 2.5-6% N_2O_3 . The heat of interaction of N_2O_3 with sulfuric acid of the concentration indicated is 20611.6 kcal/kg·mol N_2O_3 or 271.2 kcal/kg N_2O_3 . For interaction of NO_2 with sulfuric acid of the same strength, when a molecule of HNO_3 is formed from a molecule of HNSO_5 , the heat effect is 5709.5 kcal/kg·mol NO_2 or 124.1 kcal/kg NO_2 .

According to the authors quoted, the strength of the sulfuric acid has no influence on the heat effect of the process. An assessment of this work is given below.

Lopatto and Sbitneva [11], in their interesting work "Method of Calculation for Glover Towers" dwell briefly on the question of the heat effect of the denitration of nitrose and the heat of vaporization of nitrogen oxides from nitrose during desorption.

It is doubtful whether it is justifiable to compare these heat effects for these different processes, as the authors do, because the final products in the gas phase are different.

In the denitration of nitrose, where there is an interaction of nitrose with SO_2 , NO goes into the gas phase, as is also shown in the overall equation [11].

In desorption, otherwise exsorption, when no free HNO_3 is present in the nitrose, N_2O_3 goes into the gas phase, and the heat effect should naturally be different. Thus when a calculation is carried out for reaction zone of a system, the heat of denitration should be calculated according to the scheme set out in this paper, but for the reaction $2\text{HNSO}_5 + \text{H}_2\text{O} = \text{N}_2\text{O}_3 + 2\text{H}_2\text{SO}_4$ it is necessary to select the correct value of the heat effect. For calculation of the absorption zone only the heat effect of this reaction should be taken into account. We determined the differential heat of vaporization of oxides of nitrogen from nitrose by using data on the equilibrium pressure of oxides of nitrogen over nitrose.

It should be noted that a considerable amount of experimental material, accumulated recently as a result of tensimetric measurements on the systems under examination, remains at present unused.

The Clausius-Clapeyron equation makes it possible to calculate accurately the latent heat of vaporization (L), if the dependence of the vapor pressure on the temperature is known, along with the molar volume of the vapor (V_v) and of the liquid (V_l):

$$\frac{dp}{dT} = \frac{L}{T (V_v - V_l)} \quad (1)$$

When liquids are examined at temperatures far from the critical, the volume of the liquid may be neglected.

In order to simplify matters it is assumed that the vapor follows the ideal gas law and that L is constant for a given small temperature interval.

For calculations it is recommended to combine Equation 1 with the During lines, connecting the temperatures of two substances (the one being examined and a standard one) at which they have identical saturation vapor pressures. Then:

$$L = L_{st} \left(\frac{T}{T_{st}} \right)^2 \frac{dT_{st}}{dT}, \quad (2)$$

where L and L_{st} are the molar heats of vaporization of the examined and the standard substance, and T and T_{st} are the absolute temperatures of the same two substances, at which their saturation vapor pressures are identical.

In previous papers [1, 2] Kireev's equation [12] was utilized, in which the equilibrium pressures of the saturated vapor over the investigated and the standard substances are compared at identical temperatures.

If water is used as the standard substance, then

$$\log P_{N_2O_3} = Q \cdot \log P_{H_2O} + B, \quad (3)$$

where P_{H_2O} is the pressure of dry saturated water vapor at the temperature at which the equilibrium pressure of oxides of nitrogen over nitrore is determined (in mm Hg); $P_{N_2O_3}$ is the equilibrium pressure of oxides of nitrogen over nitrore (in mm Hg);

$$Q = \frac{L_{N_2O_3}}{L_{H_2O}}$$

is the slope of the straight lines in the plot of $\log P_{H_2O} - \log P_{N_2O_3}$, $L_{N_2O_3}$ and L_{H_2O} are the molar heats of vaporization of the oxides of nitrogen from water; B is the intercept, cut off on the ordinate by the extension of the straight lines uniting the experimental points in the same coordinates.

Knowing the functional dependence of L_{H_2O} on temperature, $L_{N_2O_3}$ can be found for different temperatures. Q depends on the strength of the sulfuric acid, but is practically independent of the nitrore concentration of the nitrore liquid.

In going from lower temperatures to those above 30-40°, there is a tendency for the lines on the graph ($\log P_{H_2O} - \log P_{N_2O_3}$) to change direction, due to a change of the properties of the system and conditioned, apparently, by structural changes in water when the temperature is raised. The temperature at which the lines change direction depends on the strength of the sulfuric acid, and in fact the higher this strength, the higher the temperature of direction change. In the paper in question, the authors concerned themselves only with temperatures above 30-40°.

The absence of sufficient data on the hydrolysis of nitrosyl sulfate in nitrore and of the way in which the hydrolysis is affected by temperature and the concentrations of the components, makes it impossible to recalculate the heat of vaporization taking into account the degree of hydrolysis of the nitrosyl sulfate. The values of the heat of vaporization of oxides of nitrogen from nitrore are given below without such a recalculation. This, however, should not prevent their use for technological calculations.

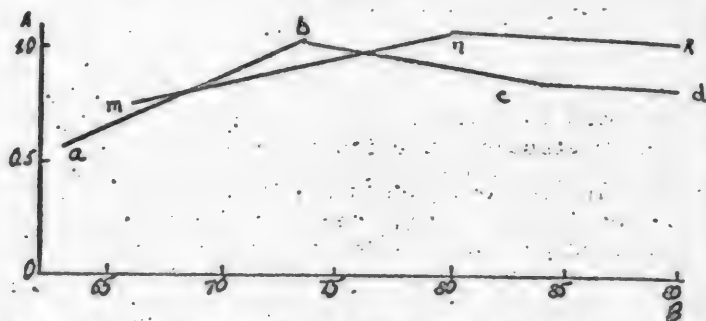
Nitrore Containing No Free HNO_3 (System H_2SO_4 , H_2O , N_2O_3)

The values of $Q_{N_2O_3}$ as a function of the sulfuric acid strength are presented in Table 1 and Fig. 1. The Point b in Fig. 1 corresponds to 73.2% H_2SO_4 ($H_2SO_4 \cdot 2H_2O$), and point c to 84% H_2SO_4 (the monohydrate).

TABLE 1

Dependence of $Q_{N_2O_3}$ on the H_2SO_4 Strength

H_2SO_4 content (in %)	$Q_{N_2O_3}$
66.....	0.694
68.....	0.778
70.....	0.865
72.....	0.950
74.....	1.014
76.....	0.981
78.....	0.948
80.....	0.915
82.....	0.883
84.....	0.85
86.....	0.842
88.....	0.835
90.....	0.827
92.....	0.82

Fig. 1. Dependence of $Q_{N_2O_3}$ on the H_2SO_4 strength.A - $Q_{N_2O_3}$; B - % H_2SO_4 . Explanation of the letters on the graph is given in the text.

For the heat of vaporization of the oxides of nitrogen from nitrose we finally obtain:

$$1) C_{H_2SO_4} \leq 73.2\% H_2SO_4;$$

$$L_{N_2O_3} = (0.04353 \cdot C_{H_2SO_4} - 2.1795) \cdot L_{H_2O} \quad (4)$$

$$2) 84\% < C_{H_2SO_4} < 73.2\% H_2SO_4;$$

$$L_{N_2O_3} = (2.2275 - 0.0164 \cdot C_{H_2SO_4}) \cdot L_{H_2O} \quad (5)$$

$$3) C_{H_2SO_4} \geq 84\% H_2SO_4;$$

$$L_{N_2O_3} = (1.165 - 0.00375 \cdot C_{H_2SO_4}) \cdot L_{H_2O} \quad (6)$$

L_{H_2O} (in kg. cal/kg·mol H_2O) values are to be found in the table at the temperature for which $L_{N_2O_3}$ values are determined.

In Table 2 and Fig. 2. are given the molar heats of vaporization of the oxides of nitrogen from nitrose, $L_{N_2O_3}$; to convert them to a weight basis they must be divided by 76.

It follows from Table 2 that, as the temperature increases, the heat of vaporization of the oxides of nitrogen from nitrose falls, and on the other hand it rises as the sulfuric acid strength increases up to 73.2%. As the strength of the acid is increased beyond that point the heat of vaporization falls, but more slowly than the rate at which it increased beforehand.

Matsui [13], using the static method and Bodenstein quartz manometer, measured the equilibrium pressure of oxides of nitrogen as the difference between the total pressure and the pressure of water vapor, from which measurements he calculated the heat of vaporization from the formula

$$L_{N_2O_3} = \frac{4.575 \cdot T_2 T_1}{T_2 - T_1} \log \frac{P_2}{P_1} \quad (7)$$

The equilibrium pressure of water vapor over nitrose was calculated from the data tabulated by Sorel, with corrections to the Rayleigh equation, and it was

TABLE 2

Molar Heats of Vaporization of Oxides of Nitrogen from Nitrore

H ₂ SO ₄ content (in %)	Molar heat of vaporization at temperatures (in °C)					
	40	60	80	100	120	140
68	8049	7891	7729	7558	7375	7177
72	9829	9636	9437	9231	9005	8764
76	10140	9940	9735	9521	9289	9041
80	9440	9280	9090	8889	8673	8441
84	8795	8620	8444	8258	8057	7841
88	8640	8470	8295	8112	7915	7703
92	8484	8317	8146	7966	7773	7565

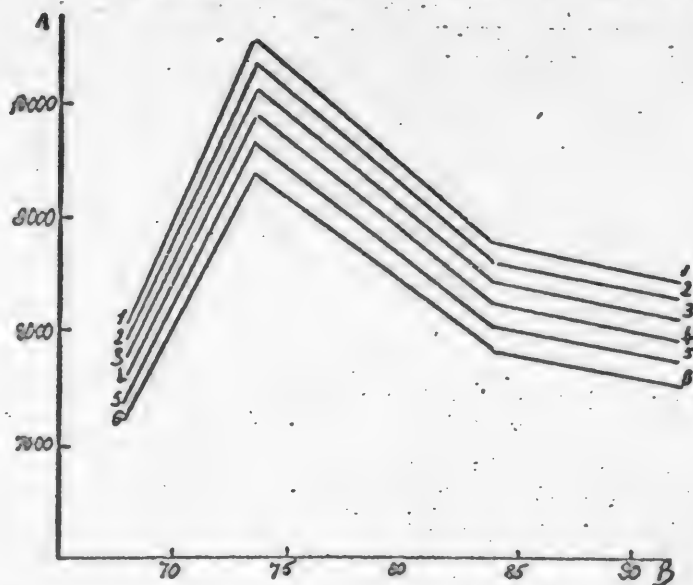


Fig. 2. Molar heats of vaporization of oxides of nitrogen from nitrore, $L_{N_2O_3}$.
 A - $L_{N_2O_3}$ (kg. cal/kg.mol); B - % H₂SO₄. Temperatures: 1 - 40; 2 - 60; 3 - 80;
 4 - 100; 5 - 120; 6 - 140.

partly checked by the condensation method. In this way an average value of 9250 kg. cal/kg.mol N_2O_3 for 70-80.8% H₂SO₄ strength was obtained.

The same value of $L_{N_2O_3}$ was found with technical nitroses, by blowing-off.

According to this investigator, the nitrore content of a nitrore is practically independent of the heat of vaporization. If a calculation is made for different concentrations of sulfuric acid, taking his data, we found that (Table 3) the heat of vaporization also varies with the concentration of acid.

In another paper [14] the erroneous assertion is made that in Matsui's equation

$$\log P = - \frac{9250}{4.571 \cdot T} + C, \quad (8)$$

where P = total vapor pressure (of H₂O and oxides of nitrogen) over the nitrore.

Actually, P should correspond only to the pressure of oxides of nitrogen over the nitrore.

TABLE 3

Effect of Concentration of Acid on
the Heat of Evaporation, from Matsui's
Results

H ₂ SO ₄ content (in %)	70.12	76.05	80.8
L _{N₂O₃} kg. cal/kg.mol	9300	9400	9250

TABLE 4

Heat of Vaporization from Data Obtained
by the Author and by Matsui

H ₂ SO ₄ content (in %)	70.12	76.05	80.8
L _{N₂O₃} according to data by Matsui	9028.8	9424	9332.8
L _{N₂O₃} according to data by the author.....	8512	9729	9272

In Table 4 are set forth our calculations using equations (4)-(6) and the data on these papers, the latter having been previously corrected with the aid of the graphs ($\log P_{H_2O} - P_{N_2O_3}$).

Berl and Saenger [15], starting from the total equilibrium pressure of oxides of nitrogen and water over nitrore, found by the static method, also calculated the molar heat of vaporization, but this would correspond to the quantity of N₂O₃ and H₂O according to their mole fractions in the gas phase.

The partial pressure of N₂O₃ and the corresponding heat of vaporization of N₂O₃ were not determined on this basis, since the authors did not know the depression of the vapor pressure of water over differ-

ent concentrations of sulfuric acid in the presence of dissolved oxides of nitrogen.

Since the composition of the gas phase varies with the strength of the sulfuric acid and the temperature, and also because the heats of vaporization of the components are different, the heats of vaporization found by Berl and Saenger should change with the strength of the acid and the nitrore content of the nitrore, as is actually observed.

In Table 5 are given the average values of the molar heats of vaporization of nitrore as a function of the strength of the acid, at a nitrore content of 0.1 mol/liter, for the temperature interval studied by them.

TABLE 5

Average Values of L_{N₂O₃} for a Nitrore Content of 0.1 mol/liter, from the
Data of Berl and Saenger

H ₂ SO ₄ content (in %)	64	67	68.5	70	73.28	75.65	78.04	80
L _{N₂O₃} , H ₂ O	8223	9383	9943	10453	11275	11650	12056	12383

From Table 5 it can be seen that as the temperature of the sulfuric acid is raised, the equilibrium pressure of the oxides of nitrogen falls more rapidly than the equilibrium pressure of water vapor over the nitrore, which also involves an increase of L_{N₂O₃}, H₂O. As a result, the molar heat of vaporization of water from sulfuric acid is higher than the heat of vaporization of N₂O₃ from the same acid.

In Table 6 the effect of the nitrore content of nitrore on the heat of vaporization at an acid content of 68.5% is shown.

It follows from Table 6 that, with increase of the nitrore content of the nitrore, the mole fraction of the oxides of nitrogen in the gas phase increases, which will also result in a lowering of the heat of vaporization.¹

¹ It should also be taken into account that a somewhat larger heat effect will be associated with the first portion of the oxides of nitrogen.

TABLE 6

Effect of Concentration of Nitrore on the Heat of Vaporization at 68.5% Sulfuric Acid Content

H ₂ O ₃ content (in mol/liter)	0	0.0258	0.05	0.075	0.1018	0.2	0.3	0.48
L _{N₂O₃, H₂O}	11014	10726	10392	10144	9943	9370	9057	8631

Starting from the vapor pressure of oxides of nitrogen over nitrore, calculated according to the equations given earlier [1, 2], making corrections for the dissociation of N₂O₃ in the gas phase into NO and NO₂ and taking the water vapor pressure as the difference between the total pressure and the calculated pressure of NO and NO₂, then the heat of vaporization, found in this way, will differ from that given by Berl and Saenger by 3-7%.

Nitroses Containing Free HNO₃. (System H₂SO₄, H₂O, N₂O₃, HNO₃).

In Table 7 and Fig. 1 are given the values of $Q_{\text{NO}, \text{NO}_2}$ as a function of the strength of the sulfuric acid [2].

TABLE 7

Values of $Q_{\text{NO}, \text{NO}_2}$ as a function of the H₂SO₄ strength

H ₂ SO ₄ content (in %)	$Q_{\text{NO}, \text{NO}_2}$
66.....	0.75
68.....	0.796
70.....	0.842
72.....	0.887
74.....	0.933
76.....	0.979
78.....	1.024
80.....	1.07
82.....	1.064
84.....	1.056
86.....	1.047
88.....	1.039
90.....	1.031
92.....	1.023

The values of $Q_{\text{NO}, \text{NO}_2}$ are practically independent of the N₂O₃ and HNO₃ contents in the nitrore, within the limits of concentration which were studied. Finally, the equations for the heat of vaporization of oxides and nitrogen from nitrore, in the presence of free acid, take the form

$$1) \text{ } C_{\text{H}_2\text{SO}_4} \leq 80\% \text{ H}_2\text{SO}_4; \\ L_{\text{NO}, \text{NO}_2} = (0.02284 C_{\text{H}_2\text{SO}_4} - 0.7572) \cdot L_{\text{H}_2\text{O}} \quad (9)$$

$$2) \text{ } C_{\text{H}_2\text{SO}_4} \geq 80\% \text{ H}_2\text{SO}_4; \\ L_{\text{NO}, \text{NO}_2} = (1.4 - 0.0041 \cdot C_{\text{H}_2\text{SO}_4}) \cdot L_{\text{H}_2\text{O}} \quad (10)$$

The value of $L_{\text{H}_2\text{O}}$ is found from tables at the temperature at which the $L_{\text{NO}, \text{NO}_2}$ values are determined.

The results of calculations using Equations (9) and (10) are set out in Table 8 and Fig. 3, the units being kcal/kg·mol NO, NO₂.

To convert the heat effects to weight units, they must be divided by the molecular weight $M_{\text{NO}, \text{NO}_2}$ where $92 < M_{\text{NO}, \text{NO}_2} > 76$ ($M_{\text{N}_2\text{O}_3} = 76$; $M_{\text{N}_2\text{O}_4} = 92$). For strong acid this molecular weight is close to 92 and for weak acid, it is close to 76.

The values of $L_{\text{NO}, \text{NO}_2}$ can be made more accurate when data on the composition of the equilibrium oxides of nitrogen over the given systems are available.

With increase of temperature, $L_{\text{NO}, \text{NO}_2}$ falls at the given acid strength.

With increase of the acid concentration at constant temperature $L_{\text{NO}, \text{NO}_2}$ increases up to ~80% H₂SO₄, and with further increase in the concentration it slowly falls, the rate of increase considerably exceeding the rate of fall.

TABLE 8

Results of Calculation of L_{NO, NO_2} According to Equations (9) and (10)

H_2SO_4 content (in %)	Molar heat of vaporization at temperatures (in °C)					
	40	60	80	100	120	140
68	8235	8070	7905	7730	7550	7350
72	9180	9000	8815	8620	8410	8185
76	10120	9930	9730	9515	9285	9033
80	11070	10860	10630	10400	10150	9875
84	10935	10720	10500	10270	10020	9750
88	10750	10540	10320	10090	9850	9580
92	10590	10380	10170	9950	9700	9445

From a comparison of the data of Tables 2 and 8 it is evident that the molar heat of vaporization of oxides of nitrogen from nitrose is, as a rule, higher in the presence of HNO_3 than in its absence.

This is particularly notable for strong acids ($>76\% H_2SO_4$) and should be explained by the non-identity of the gas phase composition in equilibrium in the two cases.

When free HNO_3 is present in the nitrose, the equilibrium composition of the oxides of nitrogen changes towards the formation, in the gas phase, of an excess of NO_2 over the stoichiometric. Besides this, the HNO_3 content in the vapor should be taken into account. According to data of separate investigators, at higher sulfuric acid concentrations this composition is very close to that for the molecule NO_2 only.

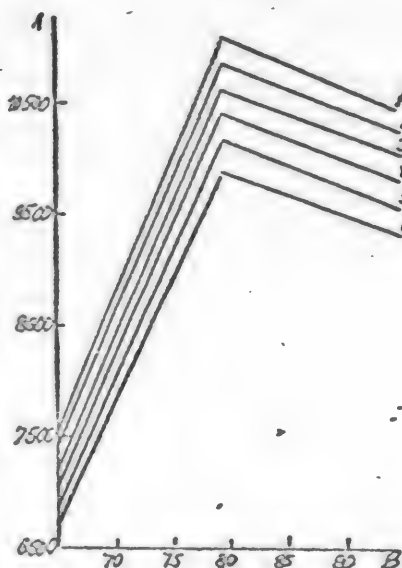


Fig. 3. Results of calculation of L_{NO, NO_2} from Equations 16 and 17.

A - L_{NO, NO_2} (kcal/kg mole); B - H_2SO_4 .
Temperatures: 1 - 40; 2 - 60; 3 - 80; 4 - 100;
5 - 120; 6 - 140.

The individual heats of vaporization of NO_2 and NO should be different and this should be the reason for the notable divergences in the heats of vaporization of the oxides of nitrogen from nitrose.

The absence of sufficient quantitative data on the composition of the equilibrium oxides of nitrogen over nitroses containing HNO_3 , makes it impossible to determine the value of the individual heats of vaporization of NO and NO_2 .

Since the heat effects obtained by Kartashev and Tseitlin differ considerably from those given by us, it is necessary to make the following remarks about this work. In it, heats of solution were given which are close to the integral ones. The solvents themselves also changed in concentration somewhat during the time of experiment.

In carrying out the experi-

ments. the process of absorption of oxides of nitrogen was obscured by a considerable number of attendant phenomena, which in total make it impossible to consider the results obtained as an answer to the problem posed.

According to Equation 1, in the absorption of 1 kg of N_2O_3 , 0.237 kg of H_2O is liberated. This leads to a dilution of the acid and the liberation of a considerable quantity of heat. If the calculation of the heat of dilution is made using, for example Thomsen's formula, then it is found to be 50% of the heat given out in individual experiments.

Furthermore, thanks to the drying of the oxides in a P_2O_5 column, the unabsorbed gas leaving the apparatus carries with it a quantity of water vapor, close to its equilibrium pressure over the acid of the given strength at the prevailing temperature. This carries away heat. The heat corresponding to the external work performed on the gas or by the gas, will be different from that which is involved in practice and in the experiments of other investigators. Since high concentrations of oxides of nitrogen in the gas phase were involved in the work in question, the concentration of undissociated N_2O_3 should be considerably larger. The latter two circumstances are of less importance than the first.

If the heat of dilution of the acid were calculated, then the results of this work would be close to those given above. For the system H_2SO_4 , H_2O , N_2O_3 , HNO_3 the results practically agree, if they are related to one and the same unit, for example, M_{NO_2} .

SUMMARY

1. An analytical expression is given for the differential heats of vaporization of oxides of nitrogen from nitrose $L_{N_2O_3} = f(C_{H_2SO_4} \cdot T)$ for the system H_2SO_4 , H_2O , N_2O_3 , and the values of these heats are calculated.

2. It has been established that $L_{N_2O_3}$ decreases with increase of temperature, does not vary with the nitrose content of the nitrose (within the limits of concentration stated) and varies with the sulfuric acid concentration up to a maximum value at $\sim 73.2\%$ H_2SO_4 .

3. An analytical expression has been found for the differential heats of vaporization of oxides of nitrogen $L_{NO, NO_2} = \varphi(C_{H_2SO_4} \cdot T)$ from nitrose when free HNO_3 is present in it, i.e. for the system H_2SO_4 , H_2O , N_2O_3 , HNO_3 . The values of these heats have been calculated.

4. It has been established that L_{NO, NO_2} decreases with increase of temperature, is practically independent of the concentration of N_2O_3 and HNO_3 in the nitrose, within the concentration limits studied, and when the concentration of sulfuric acid varies, passes through a maximum at about 80% H_2SO_4 .

5. It has been established that the molar heat of vaporization of oxides of nitrogen from nitrose in the presence of HNO_3 is higher than in its absence, for acids strong in H_2SO_4 . This should be explained by the non-identity in composition of the equilibrium gas phases in both cases.

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PHOTOGRAPHS ON OXIDIZED ALUMINUM

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Oxide layers on aluminum used for sensitization by different light sensitive substances should be colorless or white, have a definite thickness and porosity, should be chemically stable, mechanically compact and strong. The quality of the oxide layer depends to a large degree on the purity of the aluminum used or the composition of its alloy. The best oxide films are obtained from the purest kinds of aluminum, containing 99.5-99.9% Al. Very different oxidized layers may be obtained by oxidizing aluminum in different electrolytes.

By using a silver halide for sensitizing the oxide layer on aluminum, a stable silver image may be obtained [1, 2]. Photographic images obtained in the pores of oxide layers on aluminum offer extensive possibilities of use for the preparation of different kinds of scales and rules, dials, sign-boards, diagrams, maps, bases for stable reproductions and also for decorative purposes, for records, etc.

EXPERIMENTAL

Oxidation of Aluminum. Sulfuric acid was the main electrolyte used for the oxidation of aluminum, but in individual experiments chromic acid was also employed. The material to be oxidized was cold-worked aluminum foil, 0.3-0.5 mm thick, containing (in %): Al 99.4, Si 0.38, and Fe 0.3. The oxidation was carried out in a glass cell with a stirrer, the volume of electrolyte being 10 liters.

For oxidation in sulfuric acid two symmetrically placed lead plates served as cathodes, when the oxidation was performed in chromic acid these were replaced by plates of stainless steel, brand EYa-1. The aluminum plate being oxidized was the anode (usual size 9 x 12 cm) placed between the cathodes. A constant temperature was maintained in the bath (0.5°) by a special arrangement for thermoregulation with a contact thermometer and a relay.

The aluminum plate before oxidation was given a preliminary polish and was afterwards cleaned with benzene and alcohol to remove from its surface the bulk of the grease. Before the oxidation itself the aluminum was finally cleaned by treatment at 50-60° for 2-3 minutes in a solution containing 46 g of disodium phosphate, 8 g of caustic soda, and 26 g of water glass, in 1 liter of water. After washing in running water the plates were oxidized.

Oxidation was carried on in 5, 10, 15 and 20% sulfuric acid, at 20, 30 and 50° and at an anode current density of 1-2.5 A/dm². The duration of oxidation was 10-60 minutes.

For quantitative determination of the thickness of the oxide film obtained, two methods were used, sectioning and double focussing [3]. Determinations were

made with a metallurgical microscope. The sectioning method requires careful preparation of the polished section of the oxide film and takes a long time, while the double focussing method is very simple and, with sufficient practice, a film thickness can be determined with it in only 5 minutes. Comparative determinations showed that the results obtained by both methods differ very little from one another. Measurements of the thicknesses of oxide films by the intensity to which they are stained by aniline or diazo dyestuffs, though simple, are not very accurate.

For sensitizing by silver halides (see below) the best oxide layer was that obtained in 10% sulfuric acid at 30° with an anode current density of 1.5 A/dm², oxidized for 45-60 minutes. When oxidizing in 2-5 and 15-20% sulfuric acid, and also at higher temperatures the oxide films obtained were less suitable. With more concentrated solutions and at higher temperatures corrosion films were observed, and they were not so thick. In weaker solutions of sulfuric acid hard and brittle films were obtained.

The dependence of the thickness of the oxide film on the concentration of sulfuric acid, when the period of oxidation was 1 hour, the anode c.d. 1.5 A/dm² and the temperature 30°, is shown in Table 1.

TABLE 1

Effect of H₂SO₄ Concentration on the Thickness of Oxide Films

H ₂ SO ₄ concentration (in %)	5	10	15	20
Thickness of the oxidized film (in μ).....	25	25	15	10

TABLE 2

Effect of Time of Oxidation on Thickness of Oxide Film

Time of oxidation (in minutes)	15	30	45	60
Thickness of oxidized film (in μ)	5	11.5	15.0	25.0

The change in thickness of the oxide film with the time of oxidation, using 10% sulfuric acid at 30° and 1.5 A/dm² anode c.d. is shown in Table 2 and Fig. 1.

The oxide films obtained, when dried in air and by heating, showed a small difference in weight (0.002 g/dm²), indicating the small amount of moisture included in the layer.

Sensitization by silver bromide.

Simple calculation showed that activation of the oxide film by immersion in an alkali halide salt and afterwards in silver nitrate would produce an amount of silver halide in the layer which would be quite insufficient for ordinary chemical development, even in a thick oxide film. This was also confirmed by experiments, in which a non-uniform

distribution of silver in the film was also observed. The pictures obtained were frequently muddy and spotted. Repeated immersion in solutions of alkali halides, followed by immersion in silver nitrate, for sensitization was therefore studied.

Use of different alkali halides (KCl, KBr KI) for sensitization showed that when silver chloride and bromide were formed, it was visually obvious that the results were approximately identical. After prolonged sensitization, and also at higher temperatures, and after immersion in a solution of potassium iodide, corrosion films were observed. When using for activation 15-20% and more concentrated solutions of potassium bromide and silver nitrate, coarse deposits of silver bromide were formed and the sensitized layer was not uniform. It therefore seemed to be more suitable to use 10% potassium bromide and silver nitrate at ordinary temperature (20°). Rapid rinsing of the plate in water, in transfer from one solution to another during sensitization, had a beneficial effect (less

precipitation of a deposit on the surface layer), and so had rubbing of the layer during immersion of the plate in the solution. Complete drying of the plate before transfer from one solution to the other had a bad effect on the sensitization.

The thickness of the oxide layer and its porosity are extremely important factors determining the suitability of the film for photographic purposes. Knowing the thickness of the film and the "true pore volume", the maximum quantity of silver bromide which can be deposited in the pores can be calculated. To determine this true pore volume, it is necessary to know the apparent specific gravity of the oxide layer. In special experiments to obtain a pure oxide film, without the aluminum foundation, and to determine its thickness, the surface area (and hence also its volume), and weight, it was found that, in the oxide layers formed, the true pore volume was about 50% of the whole volume of the film.

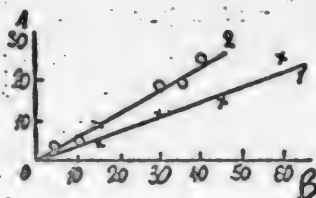


Fig. 1. Effect of time of oxidation on the thickness of the oxide film.

A - Thickness of film (in μ); B - time (in minutes).
1 - Author's data; 2 - Dahl's data.

on the number of successive immersions (n) of the plate being sensitized in the solutions of potassium bromide and silver nitrate. From an examination of the process of successive immersion of oxidized films and the precipitation of silver bromide on them, Kheinman deduced the following equation:

$$P_n = P_{\max.} (1 - \alpha^n),$$

where α = a theoretical coefficient depending on the concentrations of KBr and AgNO_3 . In our experiments (using 10% KBr and AgNO_3), α was 0.988.

Special experiments to determine the quantity of silver bromide precipitated in the oxide film as a function of the number of successive immersions in potassium bromide and silver nitrate, confirmed the correctness of this equation. In Fig. 2 are shown the theoretical and experimental data relative to the quantity of silver bromide precipitated in the pores of the oxide film, as a function of the number of successive immersions in 10% KBr and AgNO_3 . The oxide film was obtained in 10% sulfuric acid at 30° with an anode c.d. of 1.5 A/dm^2 and a duration of oxidation of 60 minutes. The thickness of the oxidized film was 25μ .

Examination of the data shows that, to get sufficient filling of the pores of the oxide layer with silver bromide, a large number of successive immersions in the potassium bromide and silver nitrate solutions must be performed. For example, after 39 successive immersions of the sensitized plate, only about a third of the volume of oxide film was filled with silver bromide. Having to make an extremely large number of immersions of the oxide film to activate it renders the process not very convenient, and, apart from this, corrodes the film, hence it is of practical importance to seek other methods of sensitizing the oxide film with silver bromide.

From what has been said above it is easy to see that, with increasing thickness of the oxide film the quantity of silver bromide formed in the film

Knowing the true pore volume, and determining from microscopic measurements (of the thickness) the volume of the film itself, the maximum quantity of silver bromide ($P_{\max.}$) which can be deposited in 1 m^2 of film can easily be calculated. If the true pore volume is designated by V_{pore} and the specific gravity of silver bromide by α_{AgBr} , then it is evident that $P_{\max.} = V_{\text{pore}} \alpha_{\text{AgBr}}$.

It is essential to know the dependence of the quantity of silver bromide precipitated in the pores of the oxide film (P_n)

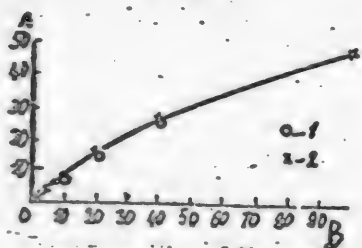


Fig. 2. Dependence of the quantity of AgBr (in g/m^2 of film) on the number of successive immersions in KBr and AgNO_3 .

A - quantity of AgBr (in g/m^2); B - number of immersions. 1 - Experimental data; 2 - Theoretical data (Kheiman's equation).

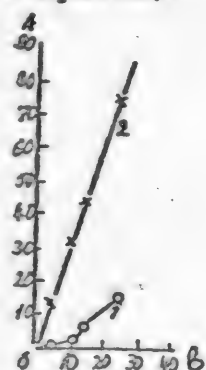


Fig. 3. Dependence on the quantity of AgBr (in g/m^2 of film) on the thickness of the film.

A - quantity of AgBr (in g/m^2); B - thickness of film (in μ). 1 - experimental data; 2 - theoretically calculated maximum quantity of AgBr ($P_{\text{max.}}$).

and then washed and dried. For chemical development amidol, metol, metol-hydroquinone and hydroquinone developers were used, prepared with different contents of developer, sulfite, and potassium bromide, but without alkali, since this attacks aluminum. In all cases the images developed, as would be expected, at different rates and the photographic properties of different developers were different. Amidol gave the highest rate of development, followed by metol; hydroquinone was slower, as was natural. The development can be carried out at a higher temperature without notable corrosion of the layer; the rate of development then increases. It was interesting that, to eliminate fogging in the development it was necessary to add potassium bromide in considerably larger quantity than usual.

increases. In Fig. 3 is shown the dependence of the quantity of silver bromide formed in the oxide film in 19 successive immersions during the time of activation, on the thickness of the film. The aluminum was oxidized for different times in 10% sulfuric acid at 30° and at 1.5 A/dm^2 anode c.d. The data obtained indicates the practical value of using a thicker oxide film in order to decrease the number of successive immersions of the oxide plate and likewise to diminish the corrosion of the film during the time of sensitization.

For photographic investigation the oxidized plates, activated with silver bromide, after drying were exposed to the light of a mercury quartz lamp ARK-2. Physical development was first used to develop the latent image formed, employing a formula for the developer published in the book by Bekunov and Shostko [4]. Later a chemical developer for the latent image was used (see below). In both cases, for physical and for chemical development of the image - even when the development was retarded, the image obtained was usually non-uniform, muddy, and spotted.

It was assumed that, in the process of deposition of silver bromide in the oxide layer, nuclei of metallic silver were formed, which also affected the purity of the developed image. Thus, if the sensitized film, immediately after activation or immediately after preliminary complete development, were to be treated with a bleaching solution, for example with potassium ferricyanide and potassium bromide, for reduction of all the silver in the layer, and afterwards washed and dried, then after exposure and development a uniform pure picture should be obtained. This was confirmed experimentally, using both physical and chemical development of the image. In later experiments, after activation of the plates, they were treated for 3-5 minutes in a bleaching solution (50 g potassium ferricyanide, 50 g potassium bromide, water to 1 liter)

As a result of the experiments carried out the following formula for amidol developer was decided on; amidol 5 g, crystallized sodium sulfite 50 g, potassium bromide 10-15 g, and water to 1 liter.

To preserve the solution better 3-5 ml acid was added (40%). With increase in the potassium bromide concentration in the developer, the light-sensitive property diminished and the time of development increased. But at the same time the fogging diminished.

The time of development at ordinary temperatures (18-20°) fluctuated between 0.5-1 and 3-5 minutes.

The use of a chemical developer made it possible to make contact prints under ordinary 300-500 W electric lamps. With a distance of 15-20 cm for a negative of average density, the exposure was in all cases 1-2 seconds, but for different layers it fluctuated considerably.

For further investigation the oxide films, as a rule, were activated by 30-40 successive immersions in 10% potassium bromide and silver nitrate at about 20°. For oxide films of about 25μ thickness this corresponds to a 25 g/m^2 of silver bromide in the film (about 15 g/m^2 of metallic silver), which considerably exceeds the amount of silver in the usual positive silver halide light-sensitive layer. A series of experiments were also carried out with thick oxide films, giving them 15-20 successive immersion in potassium bromide and silver nitrate, which in this case appears to be sufficient. Depending on the nature of the oxidation of the aluminum and the number of successive immersions during the sensitizing process (quantity of silver bromide in the layer), the color of the developed image varied from yellow to dark brown and in some cases to black. As a rule, in oxide layers of considerable thickness, obtained under more severe conditions of oxidation, and also with more highly hydrated layers, a deeper tone of the image was obtained. In comparison experiments with sensitized oxide films, obtained by oxidation in chromic acid, the color of the developed image varied from olive-black to blue-black. Physical development gave a deeper tone to the image than did chemical development.

Examination of the results of a larger number of different experiments showed that the color of the image obtained depends on the size of the particles of silver bromide in the sensitized oxide layer. With increase in the size of the particles of bromide, and of the particles of silver in the image, the tone of the latter became deeper and blacker.

Microscopic investigation of developed images at large magnifications (900-1350 x) showed that the particles of silver were oblong, with a length of the order of $0.1-0.3\mu$, lying apart from one another at average densities. As the density of the image increased the number of particles per unit surface increased, and at large densities it was not possible to distinguish separate particles of silver.

The experiments showed that even at very large densities, the images on the oxide films did not conduct electricity. From this it can be concluded that the particles of silver in the oxide layer are isolated from one another, and are located in the pores of the layer, because the oxide film itself is an insulator. Measurement of the depth at which the particles of silver in the developed image are located (microphotographically) showed that they are present in the upper layers of the oxide film. This may partially explain the small density of the images.

The color of the images obtained may be made a deeper brown or black by previous treatment of the oxide film (before sensitization) and also by sub-

sequent treatment of the sensitized layer of the developed image in hot or boiling water. It is interesting to note that if a plate, before or after the sensitization, is treated with hot water and then afterwards developed, it does not fix even on extended immersion in the fixing solution. The color of the image also deepens in the fixing bath using a hot fixing solution (in particular during hardening). A very marked deepening of the color of the developed image was observed when the sensitized plates were immersed for some time in potassium bromide solution at 35-40°, the solution being saturated with silver bromide and containing gelatine, and also in sensitization at elevated temperatures in the presence of gelatine.

The image obtained after development may be reduced, intensified or given a different tone as can the usual photographic silver image.

Sensitometric investigations of oxide layers, sensitized with silver bromide, showed that they have a small contrast coefficient. Their light-sensitivity is about 10-15 times smaller than that of the usual silver bromide photographic paper. In conclusion it can be said that the plates of shaded and half-tone image prepared thus are very effective on the polished background of oxidized aluminum. Half-tone images give good reproduction of detail.

Sensitization by diazo compounds. For sensitization by diazo compounds oxide layers were employed, which were obtained by oxidation in sulfuric and chromic acids under different conditions (see above). The sensitization was carried out at ordinary temperatures, by immersing for 5-10 minutes in a solution of p-diazodimethylaniline and R-salt. The solutions were prepared by adding, to 100 ml of distilled water, 22 g of orthophosphoric acid; the solution was heated to 80° and afterwards 3.82 g of 2,3,6-naphtholdisulfonic acid was added (R-salt). After the solution had cooled to room temperature, 3.56 g of p-diazo-dimethylaniline was dissolved in it.

To get a more uniform sensitization of the oxide layer by the solution, it was rubbed with a plug of wadding during the activation period. After dipping, the excess of solution was removed by shaking. The plates were dried with a fan. For investigating the sensitized oxide layers the latter were exposed under a mercury lamp, type ARK-2. The time of exposure at a distance of 10-20 cm was varied from 20-30 seconds to 2-3 minutes. The development was carried out in a dessicator over 20-25% ammonia solution.

As the experiments carried out showed, when oxide layers of different thickness were used, it was necessary to change the concentration of the solution for sensitization in order to get the necessary image density.

In the investigation of the dyestuff, formed in the development, it was found that it can adhere closely to the oxide layer; the duration of this process is different for different oxide layers. As a result there was obtained an image which could not be easily washed off with water, which is an essential for practical application. After development of the layer it was washed free from products of oxidation which could attack the image. The strong bonding of the dyestuff formed to the oxide layer was confirmed by experiment with pure aluminum oxide.

To obtain the necessary density of image the oxide layer should have a sufficient thickness (of the order of 10-15 μ). The light-sensitivity of the diazo layers obtained was normal. The developed image is blue or violet and is very effective on the lustrous background of the oxidized aluminum.

SUMMARY

1. In order to get a sufficient quantity of silver bromide in an oxide layer it is necessary to make repeated immersions in solutions of potassium bromide and silver nitrate.
2. The color of the developed image depends on the size of the particles of silver and on the development of the image.
3. When using diazo layers, the diazo dye formed in the development may remain firmly adherent to the oxide layer, thus giving an image which cannot be washed away by water. The duration of the process is different for different oxide films.

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CORROSION OF COPPER AND LEAD BY HYDROCARBON SOLUTIONS OF IODINE ¹⁾

L. G. Gindin and M. V. Pavlova

Extending the investigation of the corrosion of metals by non-electrolytes, we have turned our attention to hydrocarbon solutions of iodine, which appear to us to be strongly and peculiarly aggressive.

The literature on the question of the action on metals of such solutions is extremely sketchy.

Parsons [1], interested in the role of water in some chemical reactions, investigated the effect of a number of liquids, including benzene and heptane, on the reaction of magnesium, zinc, iron, antimony and silver with iodine. A mixture of the metal powder and iodine with the anhydrous liquid was made, and was left for some days in a dessicator over P_2O_5 , after which the mixture was filtered off; the iodide content of the deposit on the filter was determined. According to Parsons, reaction between iodine and metal was observed only with those liquids in which iodine dissolved. With hydrocarbons, reaction occurred only with antimony suspended in benzene, SbI_3 being formed.

As will be shown later, Parsons' results for iron in benzene solutions were not confirmed by our experiments.

Evans and Bannister [2], following the mechanism of the growth of films, investigated the action of iodine dissolved in different organic liquids and, in particular, in benzene and hexane, on silver. The samples of silver were immersed at different temperatures for 5-30 minutes in the solutions under investigation, having different concentrations, after which the investigators determined the weight of iodide and constructed curves of time against film thickness. The authors came to the conclusion that at small film thickness its rate of growth was controlled exclusively by the rate of conversion of Ag to AgI , and at larger thickness, by the diffusion of iodine through the film. However, later on Evans [3] concluded that it is not iodine which diffuses through the film but metallic silver which diffuses to the iodine.

Tikhmenev and Zvereva [4] investigated the action of 0.001 N solution of iodine in benzene on iron, Cr-Ni-steel, copper and aluminum. The experiments were carried out in "sealed" test tubes with 5 ml of solution for 30-90 minutes, after which the iodine was determined colorimetrically. Iron and copper combined in 90 minutes with all the iodine while the aluminum and the Cr-Ni-steel did not react with it at all during this time. It is curious that iodine was absorbed by the metals more rapidly from benzene than from its solutions in alcohol and potassium iodide. That is all that we have been able to find in the literature concerning this matter.

It thus appeared necessary to accumulate experimental material which would, in the first place, facilitate a qualitative description of the behavior of hydrocarbon solutions of iodine towards metals and, secondly, would give as general as possible an idea about the physico-chemical nature of this relationship.

¹⁾ Communication IX from a series of papers on the corrosion of metals by non-electrolytes.

EXPERIMENTAL

The action of iodine on copper and lead was investigated mainly in benzene and only partially in isooctane. The solvents were the same as those used in our experiments with solutions of acids [5]. Before being used they were both dried for many days over sodium and distilled from it into the flask in which the solutions were prepared.

The chemically pure iodine was purified by repeated sublimation.

The solutions were prepared as follows. The apparatus shown in Fig. 1 was assembled. The receiver was usually a glass bottle of capacity 2.5 liters, with a ground joint in its neck into which was inserted the ground connection of an automatic burette, to which were sealed two tubes with vacuum stopcocks. The apparatus was dried by passing a stream of hot dry air through it, a known weight of iodine was introduced into the bottle and the distillation of benzene into it was commenced. Since, however, iodine dissolved very slowly, the solution, with periodic agitation, was allowed to stand 2-3 days, and only after complete solution of the iodine was it titrated and automatically transferred to the test tubes (which had ground stoppers) in which the experiments were carried out. Nitrogen was used only in one special series of experiments with iron, and the results of these will be given in a subsequent paper.

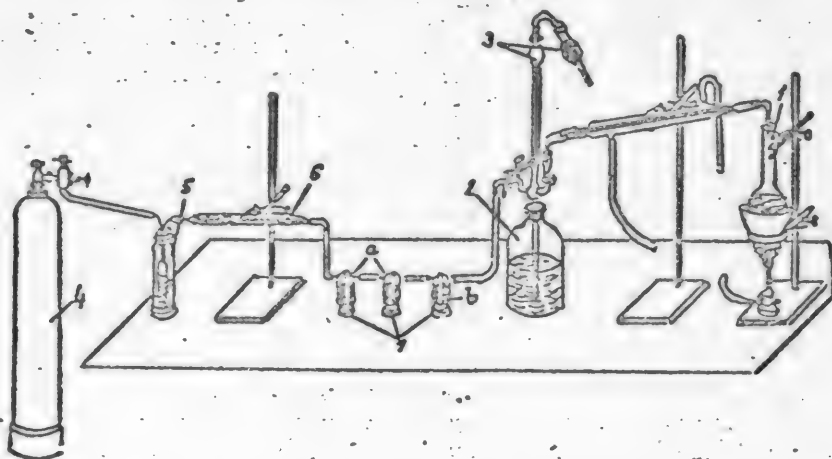


Fig. 1. Apparatus for experiments with iodine solutions.

1 - flask for distillation of hydrocarbon; 2 - bottle for iodine solution; 3 - automatic burette with a calcium chloride drying tube; 4 - nitrogen cylinder; 5 - Drexel bottle containing H_2SO_4 ; 6 - tube containing solid KOH; 7 - Tishchenko bottles: a - filled with P_2O_5 and b - filled with glass wool.

The solutions were titrated in the usual manner: 10 ml of the solution was mixed in an Erlenmeyer flask (with a ground stopper) with 50 ml of distilled water and some drops of 1% starch solution, after which it was titrated with 0.1 N thiosulfate with vigorous shaking of the emulsion until it was decolorized. As a rule 0.2 N solutions were employed.

The solution of iodine was shaken in the test tube, after which small metal plates (2 x 20 x 60 mm), ground and weighed, were suspended in it from a hook; they were completely immersed in the solution. After a more or less extensive period of contact with the solution at room temperature in diffused light, the

volume of the solution and its titer were determined, and also the loss of metal. Apart from this, the composition of the corrosion product was determined, which in a number of cases could be done quite easily by a comparison of the quantity of metal and halide reacted. These and some other data, of which more will be said later on, were usually quite sufficient to give a general idea about the character of the corrosion process being studied.

Corrosion of copper. As is demonstrated by Table 1, benzene solutions of iodine attack copper comparatively strongly. After 25 days practically all the iodine contained in the solution had reacted with the metal. The curve in Fig. 2 shows the rate of attack; a rapid increase in the first 10 days, after which it gradually tailed off as a result of the exhaustion of the halogen reserves.

TABLE 1

Corrosion of Copper¹ by Iodine Dissolved in Benzene
Quantity of original solution 70 ml, titer 0.0278 g/ml (0.2190 N)

Expt. No.	Duration of experiment (in days)	Loss of metal (in g)	Iodine reacted		Amount of iodine that should have reacted, calculated from CuI (in g)	Ratio of reacted iodine to that calculated (in %)	Remarks
			(in g)	(in % of the total quantity)			
1	5	0.0921	0.1680	8.63	0.1838	91.40	Light grey deposit on the plates, having a layered structure. After removing the majority of the deposit, the plates were rubbed with wadding moistened with alcohol. At the end of the experiments there was practically the same quantity of solution in the test tubes as at the start.
2		0.1098	0.1610	8.27	0.2192	73.45	
3		0.1883	0.3220	6.55	0.3759	85.66	
		0.1300					
4	10	0.5893	1.1060	56.83	1.1765	94.01	
5		0.6534	1.0850	55.75	1.3042	83.17	
6		0.4974	0.8820	45.32	0.9931	88.81	
		0.5800					
7	15	0.7033	1.3160	67.63	1.4041	93.73	
8		0.6608	1.2950	66.54	1.3193	98.16	
9		0.6684					
		0.6775	0.1760	60.43	1.3345	88.13	
10	20	0.8452	1.6450	84.53	1.6875	97.49	
11		0.8676	1.6870	86.69	1.7322	97.40	
12		0.8674	1.7220	88.49	1.7318	99.44	
		0.8600					
13	25	0.6909	1.3300	68.34	1.3786	96.47	
14		0.8978	1.7430	89.56	1.7925	97.24	
15		0.9636					
		0.8506	1.8900	97.12	1.9238	98.24	

For analysis of the products of corrosion, 0.5-1.0 g of deposit, previously washed with benzene and ethanol in order to desorb iodine, was dissolved in 40 ml of a mixture of equal parts of HNO₃ (1/3) and H₂SO₄ (1/2) in a beaker for electrolysis. Afterwards the solution was diluted to 150 ml with water to eliminate NO₂ vapor and was electrolyzed in a Sargent apparatus equipped with rotating elec-

- 1) The copper contained only traces of bismuth and antimony.
- 2) Here and later on averaged data are given below the bracketed figures.

trodes, the current being 1.5 A and the p.d. 2-3 volts. The electrolysis was taken as completed when, after dilution with water no further deposition of copper on the cathode was observed in the course of 15 minutes. The results of the analysis are set out in Table 2.

TABLE 2
Analysis of the Products of Corrosion of Copper in Iodine Solutions

Expt. No.	Weight (in g)	Copper found		Remarks
		(in g)	(in %)	
1	0.5000	0.1650	33.00	CuI contains 33.38% Cu, CuI ₂ contains 20.4% Cu
Mixture of 5, 6 and 7	0.5000	0.1648,	32.96,	
8	0.5000	0.1648	32.80,	
9	0.5000	0.1664,	33.28	
12	0.5000	0.1660,	33.20,	
15	0.5000	0.1672	33.44	

Judged by these results, the product of corrosion of copper is cuprous iodide. This is further confirmed by the ratio of the quantity of reacted copper and halogen. However a glance at the data of Table 1 directs attention to the definite non-correspondence between the actual loss of iodine and that indicated by the calculation, if it is taken that the whole quantity of copper in effect was converted to cuprous iodide. The interesting thing is not the non-correspondence itself, but its character: in all cases without exception the amount of iodine leaving the solution is less than that required by theory, whereas the contrary would be expected, considering its volatility, adsorption by the corrosion products, and a number of other factors which would cause a loss of iodine but not of metal. It is also surprising that the non-correspondence weakens with time - disappearing in experiments of longer duration.

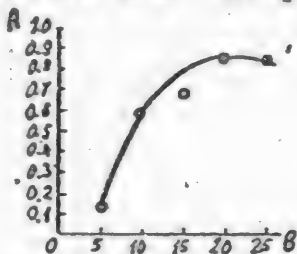


Fig. 2. Action of benzene solutions of iodine on copper.

A - loss of metal (in g); B - time (in days).

The most probable source of this peculiarity is that not all the copper that disappears is converted to iodide: it also partially combines with oxygen. Apparently, in parallel with the process of forming cuprous iodide there is an oxidation of copper by the oxygen contained in the solution and diffusing to the copper from the atmosphere, which is, generally speaking, quite natural.¹ It must be assumed that iodination stimulates oxidation, in that it facilitates the access of oxygen to the surface of the

metal, since in pure benzene there is no perceptible formation of oxide. Moreover the copper oxides did not react with iodine (iodine does not act on metal oxides²) and was mixed up with the main corrosion product - cuprous iodide. Part of the loss of copper should be ascribed to these oxides, so that the amount of iodine required to correspond to this loss is less, and so a better correspondence between the loss of metal and of halogen is obtained.

1) Prutton, Frey, Turnbull and Dlouhy [6] take a more extreme view, assuming that the process of corrosion of metals in hydrocarbon solutions of acids proceeds exclusively through the formation of an oxide.

2) The absence of reaction between iodine and iron oxide is the basis of Evans' method of isolating oxide films [3].

If this point of view is taken, then the disappearance of the non-correspondence, as the duration of experiment is extended, can be understood. The corrosion process was dominated by iodination. As time advanced the fraction of iodinated metal should have more and more exceeded the fraction oxidized, bringing about a gradual agreement of the loss of metal and halogen.

If our postulation is correct, analogous phenomena should be observed with other metals. Actually, we met with such a case in lead; we came upon a clear demonstration of the important role of oxygen in the process of corrosion with iron.

It would be a very strong and indisputable argument for the adoption of the point of view put forward, to have an indication of the presence of copper oxides among the products of corrosion. However, since rough calculation shows that the quantities of oxides contained in the deposit should be extremely small, - from a tenth to a few percent - their detection and determination present a complicated task.

We examined the action of iodine dissolved in isooctane as well as benzene on copper.

Isooctane solutions of iodine are violet, while those in benzene are brown, differing from one another in their physico-chemical properties, which made it interesting to compare their action on metals. Because iodine dissolves rather less in isooctane than in benzene, preliminary experiments were made with relatively weak solutions. The results of corresponding experiments are set out in Tables 3 and 4; judged by these, isooctane solutions of iodine attack copper to the same extent as do benzene solutions.

TABLE 3
Corrosion of Copper by Benzene Solutions of Iodine
Quantity of Solution 55 ml, titer 0.0023 g/ml (0.0191 N)

Expt. No.	Duration of experiment (in days)	Loss of metal	Reacted iodine		Amount of iodine which should have reacted, if CuI alone were formed	Ratio of reacted to calculated iodine, in %
			(in g)	(in % of the total quantity)		
1	10	0.0637	0.1265	100	0.1271	99.53
2		0.0639			0.1275	99.27
3		0.0639			0.1275	99.27

Corrosion of lead. As follows from the data in Table 5, iodine dissolved in benzene also acts fairly strongly on lead. The corrosion product of Pb was composed of golden-yellow leaves, quite soluble in hot water and in potassium iodide solution, so that without analysis it was evident that it consisted of PbI_2 . This was also confirmed by the ratio of the quantity of reacted metal to halogen. The same kind of non-correspondence was observed here as with copper, and the same remarks made earlier can be applied to this case as well.

In distinction from what was observed with copper, isooctane solutions of iodine react on lead many times more strongly than do benzene solutions (Tables 6 and 7).

SUMMARY

1. Benzene and isooctane solutions of iodine cause copper and lead to corrode, the first forming CuI, and the second PbI_2 .

TABLE 4

Corrosion of Copper by Isooctane Solutions of Iodine
Quantity of solution 55 ml, titer 0.0018 g/ml (0.0142 N)

Expt. No.	Duration of experiment (in days)	Loss of metal (in g)	Reacted iodine		Amount of iodine which should have reacted, if CuI alone were formed	Ratio of reacted to calculated iodine, (in %)
			(in g)	(in % of the total quantity)		
1	} 10	0.0539	} 0.0990	100	0.1075	92.09
2		0.0538		100	0.1075	92.09
3		0.0528		100	0.1054	93.93

TABLE 5

Corrosion of Lead ¹ by Iodine Dissolved in Benzene
Duration of experiments 50 days: quantity of solution 50 ml, titer of original solution 0.0266 g/ml (0.2096 N)

Expt. No.	Loss of metal (in g)	Iodine reacted		Iodine which should have reacted, calc. from PbI ₂	Ratio of reacted to calculated iodine (in %)	Remarks
		(in g)	(in % of the total quantity)			
1	1.0423	1.1550	86.84	1.2768	90.46	Products of corrosion of the lead were removed by boiling the sample for 30 minutes with distilled water. The samples of pure lead lost a maximum of 0.01 g. Practically the same quantity of solution remained in the test tube at the end of the process as was in it at the beginning
2	1.1476	1.3860	82.72	1.4058	98.59	
3	0.9655	1.1650	87.69	1.1823	98.54	
4	1.0723	1.2100	82.71	1.3137	92.11	
5	1.1242	1.2100	82.57	1.3772	87.86	

TABLE 6

Corrosion of Lead by Benzene Solutions of Iodine
Duration of experiments 10 days. 45 ml of solution; titer of the original solution 0.0023 g/ml (0.0181 N)

Expt. No.	Loss of metal	Iodine reacted		Quantity of iodine which should have reacted, calculated from PbI ₂
		(in g)	(in % of the total quantity)	
1	0.0109	0.0150	14.49	0.0133
2	0.0040	traces	—	0.0049
3	0.0032	traces	—	0.0039

¹) The composition of the lead was (in %) : Cu - 0.03; Fe - 0.06; Bi - 0.11; Zn - 0.14; Pb - remainder.

TABLE 7

Corrosion of Lead by Isooctane Solutions of Iodine

Duration of experiments 10 days, 45 ml of solution: titer of original solution 0.0018 g/ml (0.0142 N)

Expt. No.	Loss of metal (in g)	Iodine reacted		Quantity of iodine which should have reacted, calculated from PbI_2	Ratio of reacted iodine to that calculated (in %)
		(in g)	(in % of the total quantity)		
1	0.0601	0.0690	85.19	0.0736	93.75
2	0.0556	0.0650	80.24	0.0681	95.45
3	0.0632	0.0740	91.36	0.0774	95.67

2. Isooctane solutions act on lead more strongly than benzene ones, while their action on copper is about the same in both cases.

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CRITERIA OF THE UNIFORMITY OF DISTRIBUTION OF METAL ON A CATHODE AND METHODS FOR ITS DETERMINATION.¹⁾

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One of the important problems in electroplating is the production of coatings which are uniformly distributed on the surface.

The resistance to corrosion and, correspondingly the service life of a coating is determined by its thinnest part; hence non-uniformities in distribution of the coating on the surface of the article are the cause of a number of losses: the deposition of an excessive amount of light metal, loss of time in making this excess deposit, and the concomitant waste of electrical energy.

Non-uniformities in the distribution of the deposit in electroplating are caused by differences in the distance of the separate portions of the object being plated from the anode, and develop to different extents depending on the composition of the electrolyte, the conduct of the electrolysis process, and the geometry of the electrolytic cell and of the electrodes (anode and object being plated).

Uniform distribution of the plating is usually characterized as the so-called "throwing power", for the determination of which different methods and formulas have been worked out.

The best known and most widely used method of measurement (and formula) is that proposed by Haring and Blum, and advertized by the firm which manufactures the special "Haring cell". To get an ideal distribution of deposit on the surface of the electrode the throwing power calculated according to Haring and Blum's method, should be 80% [1].

Haring and Blum's formula has been corrected by many authors. Thus Pan [2] corrected this formula so that the ideally distributed plating corresponded to a 100% value of the throwing power. Field [3] introduced a further correction by taking the standard ratio between the electrodes as 2. Shlotter and Coxpinn [4] proposed a number of equations for the throwing power involving considerable modifications to the equations of Haring and Blum.

However all the corrections introduced into this method of calculation have been aimed at eliminating individual, obvious, but secondary deficiencies in the method, but have in no way eliminated its fundamental deficiencies.

The basic trouble with the method and formula is the subjectivism and complete empiricism in the evaluation of the capacity of the electrolyte for giving uniform coatings. The correlations of parameters in the equations mentioned are

¹⁾ Communication I of a series dealing with work in this field.

particular cases since the quantitative characteristics of the throwing power can be only taken as genuine (and then with reserve) for exactly those values and correlations of parameters, as are expressed in one or another method. None of the formulas mentioned even approximately aims at a general quantitative correlation between the parameters and the distribution of the deposit, or the current density, on the cathode surface. Naturally therefore, they cannot be utilized for the evaluation of electrolytes, and this is particularly true for the determination of the optimum technical parameters applicable to the plating of objects of a given form and size.

At the present time it is of particular technical interest to know what fraction of metal plated is deposited usefully how the current density is distributed over the object being covered, what is the average current density at which the most uniform distribution is attained, what is the best disposition of the object being plated towards the anode, etc.

One of the best pieces of work, related to the question of the throwing power, is that carried out by the Soviet investigator Sukhodsky [5] who worked out a graphical method for establishing the character of the distribution of current density as a function of the electrode separation and of the slope of the polarization curve, and likewise gave an analytical solution for the variation of current density and weight of the deposit with distance between the electrodes.

The dependence of the distribution of current density on the configuration of the electrodes, and also the effect of the cathodic and anodic polarization, was carefully investigated experimentally by Fedotov and Evstyukhin [6].

Starting in 1948, papers by Mashovets have appeared dealing with a graphical method of determining the distribution of current density on a cathode of arbitrary configuration [7].

In the evaluation of the uniform distribution of a plating, in spite of everything, one of the central questions remains unsolved, namely - what should be taken as an objective criterion for the uniform distribution of a metallic plating on the surface of the cathode. The solution of this question is of primary importance, because completely contradictory results in the evaluation of an electrolyte and of the method of operating an electrolysis can be obtained by using difference criteria.

This question of the criterion for the assessment of the equilibrium uniform plating and of its calculation should be examined through two special cases.

The first is typical for a concrete production object - the calculation of the criterion of uniformity and the determination of the optimum technological parameters for objects of definite size and configuration, being plated in a bath of definite geometry with a given electrolyte. In this case the task of determining the optimum running conditions (current density, temperature) for plating a given concrete article and of the optimum position in which to place this article relative to the anode, faces the technical man.

In the second case, which usually arises in the investigation and study of an electrolyte of this or that composition, neither the description of the article to be covered, nor its geometry, or that of the cell in which the operation is carried out, are known. None the less it is necessary to give at least an approximate quantitative evaluation of the possibility of obtaining uniform deposit from the electrolyte in question, to evaluate the effect of separate factors (concentration of the components, pH, temperature, etc.) in order to find the optimum composition of the electrolyte and the optimum running conditions, and to make a comparison with other electrolytes.

Of course, in this case an accurate solution of the problem is impossible, since the uniformity of distribution of a coating on cathode surface always depends on the geometry of the cell and of the object being plated, and these are not given.

However, for the more typical cases of electrolysis, the influence of a number of factors can be taken as identical: the effect of cathode and anode polarization, the electrical conductivity of the electrolyte, the dependence of the c.d. on the current efficiency, the distance between the electrodes and so on. On this basis it is possible to make a calculation for the approximate quantitative estimation of the uniformity of distribution of plating on the surface of the cathode, as a function of the factors enumerated.

Naturally, before such a method of calculation can be made, it is necessary to establish a criterion of uniformity. The latter cannot be selected arbitrarily, but should be a complete image of reality.

The problem of the uniform distribution of a covering is doubly a practical one. Therefore, taking into account what has been said above, the most objective quantitative criterion of uniformity (C_u) would be the relative quantity of the metal usefully employed: the ratio of the usefully deposited metal (M_d) to that of the superfluous metal (M_s) or to the total weight of metal M which is in principle not difference.

$$C_{u.1} = \frac{M_d}{M_s}, \text{ or } C_{u.2} = \frac{M_d}{M} = \frac{M_d}{M_s + M_d}. \quad (1)$$

These quantities are equal respectively, to:

$$C_{u.1} = \frac{\delta_{\min}}{\delta_{av} - \delta_{\min}} \quad \text{and} \quad C_{u.2} = \frac{\delta_{\min}}{\delta_{av}}, \quad (2)$$

where δ_{\min} = thickness for best covering or screening of the part, and δ_{av} = average thickness of covering.

Where the current yield is practically independent of the c.d.,

$$C_{u.1} = \frac{D_{\min}}{D_{av} - D_{\min}} \quad \text{and} \quad C_{u.2} = \frac{D_{\min}}{D_{av}}. \quad (3)$$

The C_u may be determined experimentally, and also by analytical or graphical calculation.

Evidently, the value of C_u will depend to a large extent, upon the geometry of the object being plated and the geometry of the cell.

In the second case, where the geometric form of the object being coated is not given i.e., when the boundary conditions are not given, the uniformity criterion should be expressed in a more generally applicable form, namely a differential one.

It is natural that in the differential form the criterion of uniformity should remain unchanged, because in the final analysis the differential equation should be written for real conditions. The ratio $C_u = M_d/M_s$ is equivalent to the ratio of the weights of deposits on a differential portion (m) to the change in weight

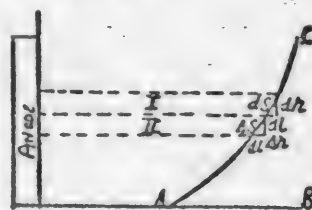


Fig. 1. Graphical process for the determination of C_u for a cylindrical cathode.

of the deposit with dm/dl :

$$C_u = \frac{m}{\frac{dm}{dl}} \quad (4)$$

For determining the value C_u we examine the case in which it is intended to coat a cylindrical object - the cathode - of area hl , and being given the equation $h = f(l)$.

Making the calculation for two separate portions of the cathode surface I and II (Fig. 1), we assume that the surface of the anode is an equipotential one and that the lines of force are straight:

$$e_{a1} + I_1 R_1 - e_{k1} = e_{a2} + I_2 R_2 - e_{k2}, \quad (5a)$$

where e_a , I , R , e_k are the potential of the anode, the current strength, the resistance of the electrolyte, and the potential of the cathode respectively.

Since we have taken that $e_{a1} = e_{a2}$, we obtain:

$$I_1 R_1 - e_{k1} = I_2 R_2 - e_{k2} \quad (5b)$$

and

$$I_1 = D ds = D \sqrt{1 + f'^2(l)} dl, \quad (5c)$$

where D = current density for the part I, ds = surface area of the part I.

$$R_1 = \rho \frac{l}{\Delta h} = \rho \frac{1}{f'(l)} dl, \quad (6)$$

where ρ = specific electrical resistance, l = distance between the anode and part I.

$$I_1 = (D + dD) \Delta s = (D + dD) \sqrt{1 + f'^2(l - dl)} dl, \quad (7)$$

$$R_2 = \rho \frac{l - dl}{\Delta h} = \rho \frac{l - dl}{f'(l - dl)} dl. \quad (8)$$

Since the potential of the cathode e_k is a function of the current density, then $e_k = \varphi(D)$ and correspondingly $de_k = \varphi'(D) dD$.

After inserting values of I_1 , R_1 , I_2 and R_2 in (4) and rearranging [8] we get:

$$\frac{dD}{dl} = \frac{D \left[1 - \frac{f''(l) l}{f'(l) + f'^3(l)} \right]}{1 - \frac{\varphi'(D) f'(l)}{\rho \sqrt{1 + f'^2(l)}}} \quad (9)$$

If the current efficiency η_k is practically constant within the limits of the c.d. employed, then it can be assumed that $m = KD$ and correspondingly that $dm = KdD$.

In this case the criterion of uniformity (throwing power) assumes the form:

$$C_u = \frac{m}{\frac{dm}{dl}} = \frac{1 - \frac{\varphi'(D) f'(l)}{\rho \sqrt{1 + f'^2(l)}}}{1 - \frac{f''(l) l}{f'(l) + f'^3(l)}} \quad (10)$$

If the article being coated is a revolving solid, then we get for C_u exactly the same value.

If the current efficiency does change with current density, then Equation 10 assumes the form:

$$C_u = \frac{1 - \frac{\varphi'(D) f'(1)}{\rho \sqrt{1 + f'^2(1)}}}{\left[1 - \frac{f''(1)}{f'(1)} \frac{1}{f'(1)} \right] \left[1 + D \frac{F'(D)}{F(D)} \right]}, \quad (11)$$

where $\eta_k = F(D)$.

In spite of the apparent complexity of Equations (9) - (11), C_u can be easily calculated if the functions $h = f(1)$, $\eta_k = F(D)$ and $e_k = \varphi(D)$, are known, because all the calculations are made by differentiation.

In cases where the potential of the anode changes sharply with c.d., Formulas (10) and (11) should be corrected. Equation (11), when the change in the potential of the anode is taken into account, takes the form:

$$C_u = \frac{\frac{\rho D l}{f'(1) D} - \varphi'(D) - \frac{\psi(D, 1) \sqrt{1 + f'^2(1)}}{f'(1)}}{1 + D \frac{F'(D)}{F(D)} \{ \psi(D, 1) f''(1) [f'(1) - 1 - f'^2(1)] - \rho \varphi_2(1) \} D}, \quad (12)$$

where

$$\varphi_2(1) = \frac{1}{f'(1)} \frac{\sqrt{1 + f'^2(1)}}{f'(1)} \left[\frac{f''(1)}{f'(1) - f'^3(1)} - \frac{1}{1} \right];$$

$$\psi(D, 1) = \varphi'_1(D_a); \quad e_a = \varphi_1(D_a).$$

For the calculation of C_u it is more convenient to use an equation related to the cathode, whose surface is inclined to that of the anode, the projection of which onto the plane hl can be described by the equation $h = a + kl$. In this case Equations (10), (11) and (12) can be considerably simplified.

Equation 10 takes the form:

$$C_u = 1 - \frac{p}{\rho} \varphi'(D), \quad (13)$$

where

$$p = \frac{k}{\sqrt{1 + k^2}};$$

and Equation 11 takes the form:

$$C_u = \frac{1 - \frac{p}{\rho} \varphi'(D)}{1 + D \frac{F'(D)}{F(D)}}, \quad (14)$$

and Equation 12 rearranged to:

$$C_u = \frac{1 + \frac{p}{\rho} \left[\varphi'_1 \frac{D}{\rho} - \varphi'(D) \right]}{1 + D \frac{F'(D)}{F(D)}}. \quad (15)$$

The optimum current density at which the maximum uniformity of plating is attained on the cathode, can be found from Equations (10) - (15) by generally known methods, by finding the limits of the relevant functions.

For solving Equations (9) - (16) it is necessary to have an equation connecting the values of e_k and D , e_a and D_a , η_k and D . More frequently the relations between these magnitudes are given in the form of graphs. In this case Equations (9) - (15) can be relatively easily solved graphically.

Equations (13) and (14) can be solved graphically as follows.

The curves $e_k = \varphi'(D)$ and $e_a = \varphi'_1(D_a) = \varphi'_1(D/p)$ are plotted, and then the values of de_k/dD and of de_a/dD_a for a series of D values, are found, e.g. by Stirling's method.

We divide the values $\varphi'(D)$ and $\varphi'_1(D_a)$ by p ; $\varphi'(D)$ is in addition multiplied by p . From these values and $\frac{1}{k}$, the values of the numerator for a series of D values are obtained.

We find by similar methods the values for the denominator for the same range of D values. Finally we obtain a series of values for C_u , corresponding to the D values. By plotting C_u against D , the optimum D value is found graphically.

The equations derived establish a quantitative dependence of the uniformity criterion on the electrical conductivity of the electrolyte, the distance between the electrodes, the nature of the cathode and anode polarization, and on the nature of the dependence of the cathode current efficiency on the current density and the curvature of the surface being plated.

The equations indicated make it possible to assess the uniformity criterion in the form presented, to compare the values of C_u in different electrolytes, and to arrive at the optimum current density.

As can be seen from Equations (10) - (15), the magnitude of the throwing power increases as $\varphi'_1(D_a)$ and $\varphi'(D)$ increases (i.e., as $\frac{de_a}{dD_a}$ and $\frac{de_k}{dD}$ increase) and

also as the specific resistance of the electrolyte decreases. The values of $\varphi'_1(D_a)$ and $\varphi'(D)$ and the electrical conductivity exert a larger influence, the smaller the distance between the cathode and anode.

The effect of the distance $\frac{1}{k}$ increases with decrease of electrical conductivity, $\varphi'_1(D_a)$ and $\varphi'(D)$. The value of $\frac{1}{k}$ is particularly important at small values of $\frac{k}{\sqrt{1+k^2}}$ i.e., at small values of the angle α (Fig. 1).

For $\eta_k = \text{const.}$ the distribution of the deposit on the cathode corresponds strictly to the current distribution. When $\eta_k = \text{const.}$ the distribution of the deposit changes. This change is quantitatively determined by the magnitude of the function, $1 + D \frac{F'(D)}{F(D)}$.

The value of the function $1 + D \frac{F'(D)}{F(D)}$ depends on the current density D , the current efficiency $\eta_k = F(D)$ and the derivative $\frac{d\eta_k}{dD} = F'(D)$.

The current density and the current efficiency can be only positive; $\frac{d\eta_k}{dD} = F'(D)$ can be either positive or negative: if $\frac{d\eta_k}{dD}$ is negative, i.e., if the current efficiency decreases as the c.d. increases, then there is a corresponding increase in the uniformity criterion: if this magnitude $\frac{d\eta_k}{dD}$ is positive, then the throwing power will diminish.

From Equations (11), (12), (14) and (15) it is evident that the larger the current density D , the larger the effect on the uniformity criterion of a change of current efficiency with current density. Increase of current density will apply a positive correction to the uniformity criterion, in those cases where the current efficiency decreases with increase in current density, and inversely.

At the same time, the higher the current efficiency, the smaller will be the effect of a change in its absolute value.

Evidently, with increase of the negative value of $D \frac{F'(D)}{F(D)}$ the value of the denominator will decrease: in cases where the value of $D \frac{F'(D)}{F(D)}$ approaches unity, the denominator inversely approaches zero, and the uniformity criterion becomes infinite, which corresponds to completely uniform ideal distribution of the plating on the cathode. If $D \frac{F'(D)}{F(D)}$ acquires a still more negative value, then the denominator in all fractions also becomes negative. The physical meaning of the negative value of the throwing power is that a larger quantity of metal will be deposited on the more distant parts of the cathode. Such cases, though rare, are met with in practice.

For the approximate determination of the uniformity criterion, the experimental method proposed by Kudryavtsev [9] is pre-eminent. The cathode is sharply bent in two places, forming 60° angles, as shown in Fig. 2. Such a form ensures complete symmetry in relation to the anodes, placed at identical distances from it. After the deposition of the plating the cathode is cut through along the lines of the apexes of the angles, and points are marked off on its sides in accordance with a special template. The thickness of the plating is measured in the middle of the cathode between the points marked out by the template. The measurement may be made by interference or in any other suitable way.

The uniformity of distribution of the covering may be assessed from the curves obtained by plotting the length of the cathode against the corresponding thickness of the covering for each part of the cathode.

Corresponding to the curves obtained, a quantitative estimate of the uniformity of the deposit may be obtained.

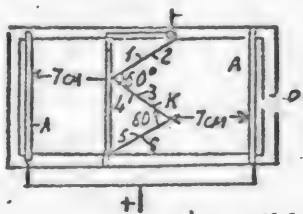


Fig. 2. Mutual arrangement of cathode and anode in the determination of the uniformity criterion by Kudryavtsev's method.

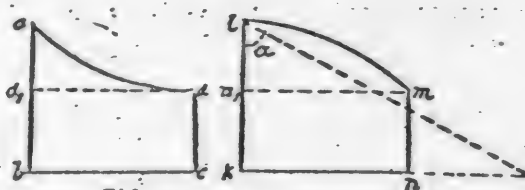


Fig. 3. Plating distribution curves obtained by Kudryavtsev's method.

However, the results obtained will depend, to a large extent, on the uniformity criterion selected.

Let us give the following example.

Assuming that, as a result of the investigation of two electrolytes by Kudryavtsev's method, we have obtained the curves for the distribution of plating

as shown in Fig. 3. Let us assume $ab = lk$ and $cd = mn$. As a quantitative criterion of the uniformity Kudryavtsev himself proposed $p_1 = \frac{q}{f} \cdot 100$ where q = thickness of the covering on the nearest part of the cathode, and f = its thickness on the farthest part.

In accordance with Kudryavtsev's criterion, the values of p_1 for electrolytes A and B are identical, in spite of the evident differences in character of the distribution between the two cases.

Other investigators applying Kudryavtsev's method, have taken as their uniformity criterion the tangent of the angle α (Fig. 3) of the right-angled triangle, whose right-angle itself is at the origin, one of whose adjacent sides is equal to q i.e. to the thickness of the plating at the nearest position of the cathode, and whose area is equal to the area bounded by the abscissa, the intercepts dc and mn and the curve of distribution of thickness of deposit itself.

It is quite evident that this criterion, based on the tangent of α , will be larger for electrolyte B, and correspondingly electrolyte B will receive a better rating.

At the same time the useless waste of metal, of electrical energy and plating time will be actually larger for electrolyte A, which shows the futility of these criteria ($p_1 = \frac{q}{f} \cdot 100$ and $\tan \alpha$).

An objective qualitative estimate of the uniformity can be obtained by using the criteria which we have proposed:

$$C_{u.A} = \frac{M_d}{M_s} = \frac{S_{bcdd_1}}{S_{add_1}} \quad \text{for electrolyte A}$$

-and

$$C_{u.B} = \frac{S_{kmm_1}}{S_{mm_1 l}} \quad \text{for electrolyte B.}$$

It is evident that the value of $C_{u.A}$ will be larger than $C_{u.B}$ and correspondingly electrolyte A will get a better rating, which is in accordance with the actual state of affairs.

The use of the objective criterion of uniformity which we have proposed, likewise has the convenience that it can be calculated using any method, experimental, analytical, or graphical.

The proposed criterion may be used for approximate evaluation of electrolytes, when neither the geometry of the object to be covered, nor the geometry of the cell, are given.

An examination of the calculation of the values of the uniformity criterion and a determination of the optimum technological parameters for objects of given size and shape will be the subject of a later paper.

SUMMARY

1. An objective criterion for the uniformity of distribution of a plating on the surface of a cathode has been proposed. It has been shown that the selection of an arbitrary criterion leads to incorrect conclusions.

2. Formulas have been derived for calculating the uniformity criterion in the most general differential form.

3. The possibility of calculating the uniformity criterion from data obtained using experimental methods (such as that of Kudryavtsev) has been demonstrated.

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THE MOVEMENT OF GAS BUBBLES DURING BUBBLING

M.A.Vitkina

The process of absorption is widely used in chemical industry and is one of the most important unit processes in chemical technology.

Of the absorption methods at present in use, bubbling is the most effective as has been shown by investigation, [1,2].

However, this process has not been sufficiently studied, and this applies specially to the upward movement of the bubbles to the surface, which plays an extremely important part in the absorption of gases and vapors.

The trajectory of gas bubbles in liquids has been studied by Obryadchikov and Khokhryakov [3] and by Stabnikov [4]. According to an investigation by Shabalin [1], the rate of rise of bubbles in an undisturbed liquid depends on their average diameter. According to a paper by Kutateladze [5], the rate of rise of bubbles also increases with their size.

Since the investigations already carried out have given discordant results, the rate of rise of gas bubbles, at different initial velocities, has been determined experimentally and theoretically as a function of their diameter.

EXPERIMENTAL

Experiments were carried out in a cylindrical glass tube, 1.2 meters long, 0.05 m diameter. The bubbles of gas were introduced from below through a glass nozzle. Nozzles of three different diameters were investigated: 3, 5, and 8 mm, these being the sizes most frequently met with in practice [1]; the height of the liquid above the nozzle was varied.

The (average) results of experiments are set forth in the Table alongside.

The following conclusions can be drawn from the experimental data: 1) the rate of rise of bubbles, for the nozzle sizes selected, lies within the limits 0.239 - 0.245 m/sec., and is practically independent of the height of the layer being bubbled: 2) with increase in the diameter of bubbles the rate of rise decreases.

Average Rate of Rise of Gas Bubbles.			
Diameter of opening d (in mm).	3	5	8
Average rate of rise of bubbles v (in mm/sec).	0.245	0.243	0.239

Equation of motion of gas bubbles. Let us consider the general case of the movement of bubbles in a given medium, at a non-zero initial velocity.

We assume that the bubbles are subject to three currents the first, called the rising current, under the influence of which the bubbles rise upwards; the second, the dynamic pressure current, also forcing them upwards; and the third current, directed downwards, is due to the resistance of the liquid.

The differential equation of movement of the bubbles under the influence of the currents indicated is:

$$\frac{\pi D^3}{6} (\gamma_1 - \gamma_g) + \frac{\pi D^2}{4} \frac{v^2}{2g} \gamma_g - \psi \frac{\pi D^2}{4} \frac{v^2}{2g} \gamma_1 = m \frac{dv}{dt}, \quad (1)$$

whence the acceleration acting on the bubbles is

$$\frac{dv}{dt} = g \left(\frac{\gamma_1}{\gamma_g} - 1 \right) - \frac{3}{4} \cdot \frac{1}{D} \left(\psi \frac{\gamma_1}{\gamma_g} - 1 \right) v^2, \quad (1a)$$

where D = diameter of the bubbles (in m); γ_1 = density of the liquid (in kg/m³)
 γ_g = density of the gas (in kg/m³) v = rate of rise of the bubbles (in m/sec.)
 ψ = coefficient of resistance: m = mass of the bubble, equal to $\frac{\pi D^3}{6} \cdot \frac{\gamma_g}{g}$;
 t = time of movement of the bubble (in sec.).

For the solution of Equation (1a) we make the substitutions:

$$a = \left(g \frac{\gamma_1}{\gamma_g} - 1 \right)$$

and

$$b = \frac{3}{4} \cdot \frac{1}{D} \frac{\psi \gamma_1 - \gamma_g}{\gamma_g} \cdot \frac{\gamma_g}{g(\gamma_1 - \gamma_g)} = \frac{3}{4} \frac{1}{g \cdot D} \cdot \frac{\psi \gamma_1 - \gamma_g}{\gamma_1 - \gamma_g}.$$

whence

$$\frac{dv}{dt} = a(1 - bv^2). \quad (2)$$

Representing the rate of movement as a function of the depth of bubbling

$$v = \frac{dH}{dt}, \quad (3)$$

where H = depth of bubbling (in m).

Using equations 2 and 3, we obtain:

$$dH = \frac{v dv}{a(1 - bv^2)}. \quad (4)$$

Integrating we obtain,

$$H = -\frac{1}{2ab} \ln(1 - bv^2) + C. \quad (5)$$

Finding C for $H = 0$ and for $v = v_1$,

$$C = \frac{1}{2ab} \ln(1 - bv_1^2).$$

thence

$$H = \frac{1}{2ab} \ln \frac{1 - bv_1^2}{1 - bv^2}. \quad (6)$$

since

$$\frac{1 - bv_1^2}{1 - bv^2} = e^{2abH},$$

the variable rate of rise of the bubbles will be:

$$v = \frac{1}{\sqrt{b}} \sqrt{1 - (1 - bv_1^2) e^{-2abH}}. \quad (7)$$

The magnitude of the final rate can be found for the condition $dv/dt = 0$ i.e., when the acceleration on the bubbles, which is always decreasing, becomes zero. At this point the rate of rise of the bubbles reaches a maximum and then remains constant.

According to Equation 2 we have:

$$a(1 - bv_f^2) = 0$$

The value of a cannot be zero, hence we have:

$$1 - bv_f^2 = 0,$$

whence

$$v_f = \frac{1}{\sqrt{b}} \quad (8)$$

Substituting for the value of b we obtain:

$$v_f = \sqrt{\frac{4}{3} D \cdot g \frac{\psi_1 - \psi_g}{\psi_1 - \psi_g}} \quad (9)$$

Using Equations (7) and (8), substituting the expanded expressions for a and b and neglecting ψ_g in comparison with ψ_1 , we obtain an equation for the variable rate of rise of the gas bubbles in the form:

$$v = \sqrt{\frac{4 \cdot D \cdot g}{3 \cdot \psi}} \left(1 - e^{-\frac{3 \psi \psi_1}{2 \cdot \psi_g} \frac{H}{D}} + v_1^2 e^{-\frac{3 \psi \psi_1}{2 \cdot \psi_g} \frac{H}{D}} \right) \quad (10)$$

A particular case of equation 10 is the expression for the variable rate of rise of bubbles when the initial velocity $v_1 = 0$.

$$v = \sqrt{\frac{4 D \cdot g}{3 \cdot \psi}} \left(1 - e^{-\frac{3 \cdot \psi \cdot \psi_1 \cdot H}{2 \cdot \psi_g \cdot D}} \right) \quad (11)$$

Analyzing the data obtained, we come to the following conclusions: 1) From Equation (9) it is evident that the final velocity v_f does not depend on the initial velocity v_1 . 2) From Equations (7) and (8) it follows that the variable rate of rise of the bubbles v theoretically approaches a constant final rate only when $H = \infty$. 3) The variable rate v in practice becomes equal to the final rate v_f at extremely small heights of the bubbling layer H .

At $H = 0.001$ m, $D = 0.008$ m, $\psi = 1.78$ (experimental data) and $v_1 = 10$ m/sec.

$$v = \sqrt{0.059} (1 - e^{-265}) + 100 \cdot e^{-265} = 0.243 \text{ m/sec.}$$

Consequently v at any height does not depend on the initial velocity, and only at very large values of v_f (practically unattainable) can some dependence of v on v_1 be found. 4) From Equation (6) the critical value of the bubbling layer height H_{cr} may be determined, at and above which the constant final value of the velocity v_f is attained.

The equation for H_{cr} takes the form:

$$H_{cr} = \frac{1}{2ab} \ln \frac{1 - bv_1^2}{1 - bv_f^2} \text{ M.} \quad (12)$$

From this equation the value of H_{cr} for v_1 between 10-20 m/sec. is found to be a fraction of a millimeter.

SUMMARY

1. Of the methods used in chemical industry for absorption, bubbling has

shown itself to be one of the most effective.

Among the factors controlling the process of bubbling, insufficient attention appears to have been paid to the upward rise of the bubbles, which plays an important part in determining the intensity of absorption of gases and vapors.

2. Investigation of the movement of gas bubbles in a given medium has shown that the rate of this movement depends, on the main, on their diameter and that at the commencement of their rise they are acted upon by an acceleration which is determined only by their density of the gas and the liquid.

3. From the equations for the variable and the final rate of rise of the bubbles, deduced in this paper, it follows that the variable rate becomes practically equal to the final rate at extremely small bubbling heights. The final rate v_f does not depend on the initial rate of the gas bubbles.

4. The equations permit the calculation of the critical height of the bubbling layer H_{cr} , at and above which the final rate of rise of the gas bubbles is attained.

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VINYLATION OF CELLULOSE

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The vinyl ethers $[R-O-CH=CH_2]$, where $R = CH_3, C_2H_5, (CH_3)_2-CH=CH_2, C_6H_5$ etc] have recently been the subject of increased investigation. These ethers, containing the unsaturated vinyl group, easily polymerize to give different polymers depending on the conditions of reaction, the catalyst etc; these polymers are coming into use as plastics, lacquer bases, adhesives etc. [1]. Hill and Pigeon [2] and others [3], have shown that, in the presence of an acid as catalyst, acetylene reacts with alcohols to form acetals, through the intermediate formation of vinyl ethers, as follows:-



and



It has been shown [4,5] that in the presence of strong alkali as catalyst, monohydric alcohols add to acetylene, to form vinyl ethers. Favorsky [4], Favorsky and Shostakovsky [6] worked out a convenient method for the preparation of vinylalkyl ethers, by the action of acetylene on alcohols under pressure in the presence of caustic potash.

It appeared to us as being not without interest to confirm Favorsky and Shostakovsky's reaction on more complicated compounds, and in particular, on cellulose. At present quite a large number of cellulose ethers are known, the methyl [7], ethyl [8], propyl [9], isobutyl, hydroxyethyl, [10], benzyl [11], glyceryl [12] and a number of other ethers have been obtained. The methyl and benzyl-celluloses have found practical application in the manufacture of plastics, lacquers, insulating materials, etc. Favorsky, Ivanov and Zaitsev [13] carried out experiments on the vinylation of cellulose and obtained products which, they suggested, were a mixture of mono-, di-, and tri-vinyl cellulose ethers.

EXPERIMENTAL

The experiments on vinylation were carried out with refined sulfite cellulose, containing 1% lignin and 5.1% moisture.

The reaction was carried out at 130-175° in a rotating autoclave under acetylene pressure, in the presence of 20-40% KOH. The duration of the experiments was varied from 18-75 hours. The vinylation yielded a fibrous product (mainly), and a resinous product dissolved in the aqueous liquor.

The liquor was acidified with 2N HCl to a weak acid reaction and extracted with ether. After the extraction the weakly acid solution was adjusted to a strong acid reaction with HCl and then extracted again with ether. The results of the experiments are shown in Table 1.

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Even in the hydrolysis of the ethereal extracts under the more severe conditions imposed by the use of 10% H_2SO_4 , no perceptible amount of CH_3CHO was observed. 1.36 g was used for hydrolysis which was carried on for 3 hours. 1.25 g, or 92%, remained after hydrolysis. The elementary compositions (in %) were: before hydrolysis C 57.9, H 6.5; after hydrolysis, C 56.8, H 6.3%. The residue did not dissolve in Schweitzer's reagent.

Vinylation of cellulose in butanol. To find out the effect of solvent on the acetylene addition reaction, cellulose was vinyolated in the presence of butanol. The conditions were the same as in the presence of water.

TABLE 2

Elementary Composition of the Products of vinyolating Cellulose

Expt No.	Description	Ashless weight (in g)	Amount (in g) of		Found (in %)		Remarks
			CO_2	H_2O	C	H	
II	a) Fibrous product	0.0894	0.1408	0.0486	43.0	6.1	Product washed with water and alcohol and dried at 105°, ash content 3.2%
		0.1018	0.1896	0.0572	43.0	6.2	
	b) Ethereal extract from weakly acid lye	0.1408	0.3459	0.0958	67.0	7.6	
		0.1430	0.3492	0.0978	66.7	7.6	
	c) Ethereal extract from strongly acid lye	0.1422	0.3270	0.0894	62.7	7.0	
		0.1350	0.2974	0.0842	62.5	7.0	
III	a) Fibrous product	0.0860	0.1526	0.0482	48.4	6.3	Product washed and dried with water and alcohol, and dried at 105°, ash content 2.3%
		0.0872	0.1542	0.0510	48.2	6.4	
	b) Ethereal extract from weakly acid lye	0.1302	0.3196	0.0844	66.0	7.3	
		0.0944	0.2238	0.0634	67.0	7.5	
	c) Ethereal extract from strongly acid lye				60.1	7.4	
					60.2	7.3	
IV	Fibrous product	0.1288	0.2581	0.0714	54.7	6.2	Extracted from strongly acid lye
	a) heavy portion	0.1250	0.2478	0.0706	54.7	6.2	
	b) light portion	0.0876	0.1702	0.0508	52.9	6.5	
		0.0696	1.1338	0.0414	53.0	6.7	
	c) ethereal extract from lye	0.1278	0.2372	0.0810	61.5	7.1	
		0.1422	0.3028	0.0890	61.0	7.0	
V	Ethereal extract from lye	0.1176	0.2684	0.0754	62.4	7.1	
		0.0934	0.2134	0.0592	62.3	7.1	

1) Theoretical figures for the following vinylation products:

$[\text{C}_6\text{H}_7\text{O}_2 (\text{OH})_2 (\text{OCH} = \text{CH}_2)]_x$	Calculated %:	C 51.1%	H 6.4%
$[\text{C}_6\text{H}_7\text{O}_2 (\text{OH}) (\text{OCH} = \text{CH}_2)_2]_x$	"	56.1	6.7
$[\text{C}_6\text{H}_7\text{O}_2 (\text{OCH} = \text{CH}_2)_3]_x$	"	60.0	6.7

TABLE 3

Determination of the Vinyl Groups in the Samples

Description of product	Weight (in g)	Quantity of NaHSO_3 (in ml)	Quantity of 0.1 N I_2 (in ml)		Quantity of CH_3COH group separated	Quantity of hydroxyl replaced
			blank	test		
Fibrous product II	0.56	5.0	16.2	8.6	0.0193	0.15
Fibrous product III	0.58	10.0	32.5	5.7	0.062	0.46
Fibrous product IV, floating portion	0.6949	1.2	18.0	8.0	0.022	0.14
ditto, heavy portion	0.8124	1.21	18.1	2.1	0.036	0.20

The butanol was distilled off from the reaction mixture after the experiments, and the vinyl ether was also extracted with ether after the residue had been acidified, as shown in Table 4. The elementary compositions of the products obtained are shown in Table 5.

TABLE 4

Vinylation of Cellulose in Butanol

Expt No.	Temperature (in °)	KOH (%)	Weight of cellulose (g)	Duration (hrs)	Product obtained	Yield of ether fraction (in % of cellulose)	Remarks
VI	130	20	50	33	1) Lye 2) Fibrous mass	60 25	Extraction made from strongly acid residue
VIa	130	20	50	33	1) Lye 2) Fibrous mass	30 -	Extraction made from weakly acid residue. Fibrous mass washed with alcohol and water.

DISCUSSION OF THE RESULTS

The action of acetylene on cellulose under the conditions of the Favorsky - Shostakovsky reaction, yielded: 1) products extracted by ether from the acidified liquor and a fibrous mass; and 2) a fibrous product insoluble in ether or alcohol, seen under the microscope to be composed of fragmentary fibers.

The fibrous product from Expt. III quite closely corresponds in elementary composition to 0.5 C_2H_2 added to one cellulose unit, i.e., to 1 mol of C_2H_2 added to $2[\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3]$ residues.

Expt. III, Found %: C 48.3; H 6.35.

$\text{C}_2\text{H}_2 \cdot 2\text{C}_6\text{H}_{10}\text{O}_5$. Calculated %: C 48; H 6.29. Fibrous product of Expt. IV, corresponding in composition to 1.5 C_2H_2 added to 1 cellulose unit.

Floating product, Found. %: C 52.95; H 6.6.
 Heavy product " " %: C 54.65; H 6.2
 $3C_2H_2 \cdot 2C_6H_7O_2(OH)_3$. Calculated %: C 53.7; H 6.47.

TABLE 5

Elementary Composition of the Products of Vinylating Cellulose in Butanol

Expt No.	Description of product	Ash content (%)	Ash-less weight (g)	Amount (in g) of:		Found (%)		No. of hydroxyl groups substituted ¹
				CO ₂	H ₂ O	C	H	
VI	1) Extract from strongly acidified lye	0	0.0876	0.2088	0.0600	65.0	7.8	1 OH-group
			0.0890	0.2118	0.0612	64.9	7.7	
	2) Extract from fibrous mass		0.0974	0.2242	0.0608	61.5	7.0	
			0.1010	0.2270	0.0635	61.3	7.0	
VIa	1) Extract from weakly acidified lye		0.1022	0.2572	0.0754	68.9	8.3	0.64 OH-group
			0.1054	0.2680	0.0792	69.2	8.4	
	2) Fibrous mass, washed with water and alcohol		0.0930	0.1998	0.0668	58.6	6.8	
			0.0960	0.2046	0.0684	58.7	6.8	
3) Extract from fibrous mass	0.1008		0.2430	0.0670	66.7	7.4		
	0.1026		0.2482	0.0696	65.9	7.6		

¹) Calculated for the CH_3COH group separated.

Hennion, Killian et al [14], showed that in the presence of an acid catalyst, alkylacetylenes add two molecules of a monohydric alcohol, forming ketals, this reaction proceeding through the intermediate formation of the corresponding vinyl ethers. Gerstein and Shostakovsky have demonstrated the ease of addition of alcohols to vinyl ethers in the presence of an acid as catalyst, and even in the absence of any catalyst, under pressure [15].

With glycol the addition of acetylene in the presence of an acid involves the intermediary formation of a cyclic acetal.

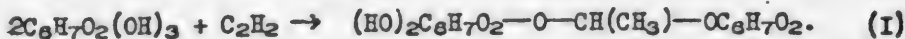
When KOH is used, Favorsky and Shostakovsky found, besides glycol divinyl ether, also ethylidene glycol, doubtless as a result of the isomerization of the initially formed monovinylglycol ether.

The authors [17] obtained triethylidene mannite in the vinylation of mannite in the presence of 10% KOH. They also established that the main products of the reaction were those formed by addition of acetylene to two or more molecules of mannite with the formation of a crosslinked ethylidene bridge; and the addition of acetylene to two hydroxyls of one molecule with the formation of cyclic acetals.

In the vinylation of cellulose three things may happen: 1) addition to acetylene of one hydroxyl; 2) addition to the molecule of acetylene of two hydroxyls of adjacent chains, forming an ethylidene bridge; and 3) addition to the molecule of acetylene of two hydroxyls of one and the same group with the formation of cyclic acetal groupings.

The second and third cases may occur simultaneously.

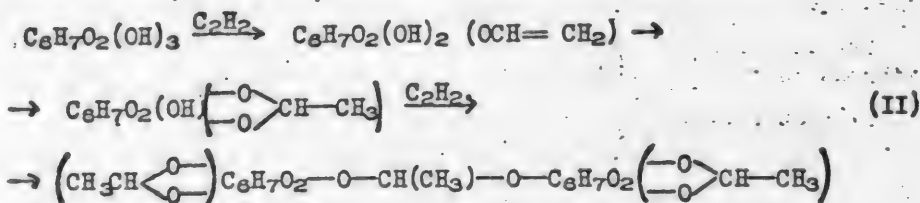
None of the vinylated celluloses added bromine, and consequently vinyl groups were not present. Thus the formation of Product III can be explained according to the scheme:



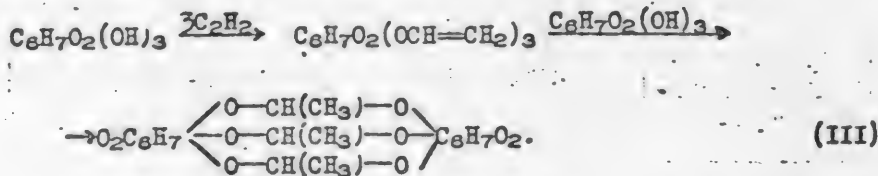
Hydrolysis gave acetaldehyde in quantity corresponding to the formation of an addition product according to this scheme.

The fibrous vinylation product in Expt. IV, as already mentioned above, corresponds to the composition $3C_2H_2 \cdot 2C_6H_7O_2(OH)_3$.

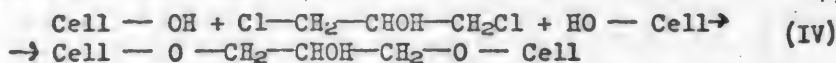
The formation of this product can occur along one of two paths:



or



The fibrous product of Expt IV did not dissolve in ether or alcohol, did not completely hydrolyze, and the hydrolysis residue did not dissolve in Schweitzer's reagent. This suggests that the vinylation proceeds by Scheme III where a large number of cross linked ethylidene bonds are formed. Shorygin and Rymashevskaya [18] obtained the glycerol ethers and showed that in the presence of a small amount of glycerol α, δ -dichloroglycin an insoluble product was obtained, as a result of the formation of cross linked bonds at the expense of the secondary alcoholic groups of glycerol, according to the scheme:



Exactly the same thing is known for polyformals and polyacetals, obtained in the acetalization of polyvinyl ethers to lower their solubility in water and to increase their stability [19]. These results likewise support the suggestion that vinylation proceeds according to Schemes II and III.

It is true that these conclusions are preliminary ones, since in the literature, as far as we know, there is not sufficient information relative to the stability of cyclic acetals of the ethylidene glycol type, a matter which should be the object of further investigation.

The products of vinylation of cellulose in butanol are, evidently, the products of the interaction of vinyl ethers with butyl alcohol. They were not subjected to more detailed investigation.

The ether-soluble products were likewise not investigated in more detail; no doubt they were attacked by the polymerization products of acetylene itself, which are obtained on heating the latter in aqueous alkali, particularly at 175°.

From the experiments which we have carried out it is evident that the vinylation of cellulose is more complicated than was supposed by Favorsky, Ivanov and Zeitsev. Vinyl ethers were not obtained, but instead products of the further transformation of cellulose, involving the formation of acetals or, as a result of addition to two adjacent chains, of ethylidene bridges, or of cyclic acetals, or of one or the other simultaneously.

SUMMARY

1. As a result of the interaction of cellulose and acetylene in the presence of an aqueous solution of KOH, products are obtained, corresponding in composition to: $2C_6H_{10}O_5 \cdot C_2H_2$ and $2C_6H_{10}O_5 \cdot 3C_2H_2$.

2. The possible structures of the vinylation products are discussed.

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SOLUTIONS OF ACETYLCELLULOSES WITH DIFFERENT ACETYL NUMBERS

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Recently one of us [1] reported data showing that the specific viscosity of one and the same acetylcellulose in different solvents may vary by a factor of more than 2. At the same time the specific gravity of the dissolved acetylcellulose and its specific volume in solution change.

The specific viscosity η_{sp} of a solution of acetylcellulose is lower, the greater the volume contraction in solution Δv_{sp} , and the greater the calculated specific gravity of the acetylcellulose in solution, d_0 . It was suggested that the magnitudes of η_{sp} , Δv_{sp} and d_0 for different acetylcelluloses depend on the intensity of the interaction of the functional (polar) groups of acetylcellulose (OH and OCOCH_3) with the polar groups of the solvents. The stronger this interaction, the lower η_{sp} and the larger Δv_{sp} and d_0 .

In another work [2] it was shown that when the same secondary acetylcellulose is dissolved in a mixture of two components, one of which (or both) is unable to dissolve the given acetylcellulose, but only causes it to swell, a considerable decrease of η_{sp} and an increase of d_0 are observed.

An increase of the interaction of acetylcellulose with a mixture of two liquids can be explained by a dissociation of the molecule of the strongly associated, active, "non-solvent" in the binary mixture; the interaction of the free polar groups of the molecule of the non-solvent with the functional groups of the acetylcellulose is thereby increased.

In this paper we give the results of a very much more extended investigation, covering acetylcelluloses with acetyl numbers from 49 to 61.4%.

EXPERIMENTAL

All acetyl-celluloses were obtained from one and the same primary acetylcellulose, prepared by homogeneous acetylation. The solution of this acetylcellulose in the acetylating mixture (syrup) was subjected to a rapid precipitation or "ageing" in order partially to saponify the acetyl groups, with subsequent precipitation.

Since all samples of acetylcellulose were obtained from the same syrup and the precipitation was carried out cautiously at lowered temperatures, it may be taken that the molecular weight of all the material obtained is approximately the same, i.e., in all samples the dimensions of the separate macromolecules are approximately identical. In this way the following acetylcelluloses were obtained:-

			Per $\text{C}_6\text{H}_{10}\text{O}_2$ unit;	
Acetylcellulose I	61.4%		3.0	0
" "	II 58.2		2.725	0.275
" "	III 55.6		2.512	0.488
" "	IV 53.7		2.382	0.618
" "	V 51.9		2.274	0.726
" "	VI 49.9		2.17	0.87

These acetylcelluloses were dissolved in different solvents in the usual manner; the viscosities of solutions containing 1, 2, 5, 10, 20 and 50 g/liter of material were measured in a capillary viscosimeter.

In Table 1 information about the solubility of Materials I-VI in different solvents is given, and in Tables 2 and 3 data about the specific viscosity of the solutions containing 2 and 20 g/liter of material.¹⁾

Acetone, acetone/ethyl alcohol (85/15), formic acid/water (80/20), dichlorethane/ethyl alcohol (85/15) and methylene chloride were used as solvents.

Since the chain length of the acetylcellulose molecules in all experiments was approximately the same, considerable differences in the measured specific viscosities can be explained only by a change of the form of the flexible molecules in solution.

The data set out earlier confirmed that the specific viscosity of acetylcellulose in solution is lower, the stronger the interaction of the polar groups of the material with those of the solvent.

In our experiments Acetylcellulose I only contained polar acetyl groups of the OCOCH_3 type. The remaining Acetylcelluloses (II-VI), apart from the OCOCH_3 groups, contained 0.275 - 0.87 OH groups per $\text{C}_6\text{H}_{10}\text{O}_5$.

TABLE 1

Solubility of Different Acetylcelluloses as a Function of Their Acetyl group content.

Solvent	% acetyl group					
	61.4	58.2	55.6	53.7	51.9	49.9
Acetone	-	+	+	+	x	o
Acetone/ alcohol	-	o	+	+	+	x
Formic acid/ water	+	+	+	+	+	x
Dichlorethane/ alcohol	-	o	+	+	+	o
Methylene chloride	+	+	o	-	-	-

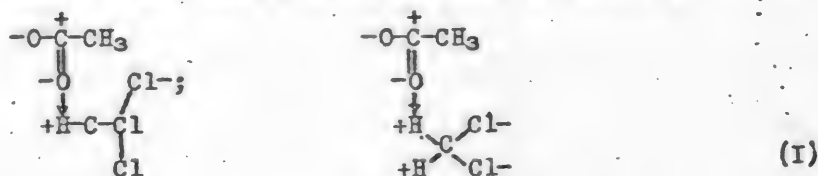
Note: The following signs have been used in the Table: + = completely dissolved; x = almost completely dissolved, traces remain; o = incompletely soluble; - = did not dissolve (swelled).

TABLE 2

Specific Viscosities of Solutions of Acetylcellulose. Concentration of Solutions 2 g/liter ($\sim 0.2\%$).

Solvent	% acetyl groups					
	61.4	58.2	55.6	53.7	51.9	49.9
Acetone	-	0.372	0.346	0.373	-	-
Acetone/alcohol	-	-	0.364	0.379	0.422	-
Formic acid/water	-	0.554	0.533	0.550	0.564	-
Dichlorethane/alcohol	-	-	0.266	0.384	0.395	-
Methylene chloride	0.576	0.606	-	-	-	-

As Clement showed, chlorinated hydrocarbons (CH_2Cl_2 , CHCl_3 , $\text{C}_2\text{H}_4\text{Cl}_2$, $\text{C}_2\text{H}_2\text{Cl}_4$) only react with acetyl groups (1 mol per 1 OCOCH_3 residue) as follows:-



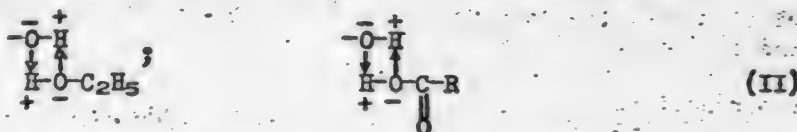
¹⁾ The specific viscosities of these solutions at concentrations of acetylcellulose of 1, 5, 10, and 50 g/liter are not given because they were not greatly different from those for solutions containing 2 and 20 g/liter.

TABLE 3

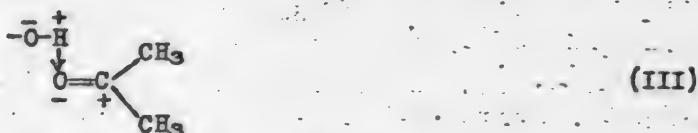
Specific Viscosities of Solutions of Acetylcellulose. Concentration of Solutions 20 g/liter (~2%).

Solvent	% acetyl group					
	61.4	58.2	55.6	53.7	51.9	49.9
Acetone	-	15.53	11.09	13.42	24.73	-
Acetone/alcohol	-	-	11.14	13.14	26.00	-
Formic acid/water	-	17.15	13.56	15.64	18.20	-
Dichlorethane/alcohol	-	-	8.95	11.68	16.79	-
Methylene chloride	6.36	10.48	-	-	-	-

According to this author also, the hydroxyl groups of secondary acetylcelluloses interact with the OH groups of alcohols or fatty acids thus:

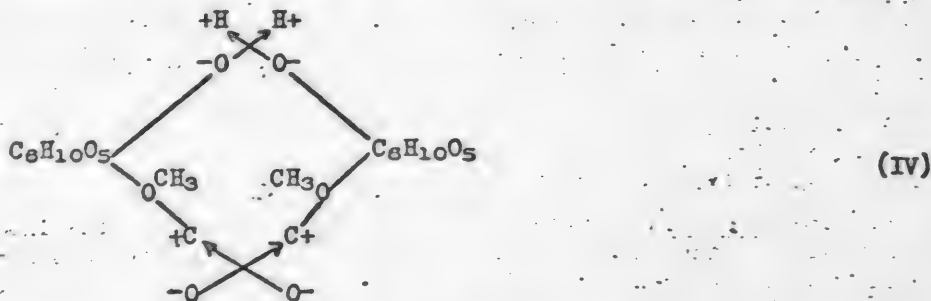


V.N. Nikitin [4] showed that in a solution of secondary nitrocellulose in alcohol/ether and in acetone the OH groups of the cellulose ether react according to Scheme II and also as follows:



Many authors [5], observing the difference in solubility of acetylcelluloses with different acetyl numbers in mixed solvents (acetone/benzene, acetone/alcohol, acetone/water, etc.) also explain the difference in behavior of the acetylcellulose by the fact that one or both types of polar groups of acetylcellulose can interact with solvent molecules to some extent.

It must also be borne in mind that the polar groups of acetylcellulose, not attracted by the solvent molecules, tend to interact with one another [4] as follows:



This interaction considerably lowers, or in general prevents, the solution of acetylcellulose solvents in which one of the polar groups (OH or OCOCH_3) remains unsolvated by the solvent molecules.

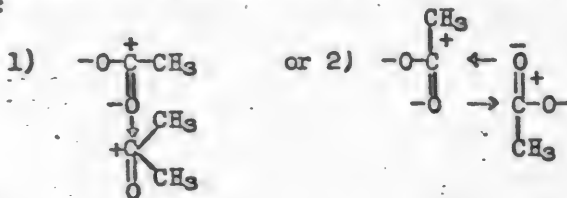
On this basis the data about the differences in specific viscosity of acetylcellulose in different solvents can be explained. The lower the η_{sp} of the acetylcellulose solution, the more vigorous is the process of solution, the weaker the intermolecular bonding according to Scheme IV, and the stronger the interaction

of the polar groups of acetylcellulose with the polar groups of the molecules of solvents according to Scheme I, II or III.

DISCUSSION OF THE RESULTS AND CONCLUSIONS

1. Methylene chloride interacts with acetyl groups of acetylcellulose only according to Scheme I. It does not react with the hydroxyl groups of acetylcellulose. Hence only the Triacetylcellulose I, which does not contain any OH groups can have all its polar groups solvated. As the number of OH groups in the acetyl cellulose which do not interact with CH_2Cl_2 increases, the number of free (non-solvated) polar groups increases and in the same way the possibility of inter-molecular combination according to Scheme IV increases. The solubility of acetylcellulose in methylene chloride deteriorated at the same time and the specific viscosity increases in those cases where the material goes into solution.

2. Acetone interacts both with the acetyl and with the hydroxyl groups of acetylcellulose, the interaction with the OH groups containing positively charged H atoms is stronger (cf. Scheme III). Triacetylcellulose I with a fairly long macromolecule cannot dissolve in acetone under the usual conditions because of the two reactions:



The second reaction, Scheme IV, occurs to a greater extent because of the larger size of the macromolecules and their similarity in the initial solid substance.

With increase in the quantity of OH groups in the acetylcellulose the interaction of these groups with molecules of acetone according to Scheme III increases and at the same time the interaction of the OH groups of neighboring acetylcellulose macromolecules with one another also increases. On account of the opposing effects of these reactions, when the number of OH groups in the acetylcellulose is still small, their interaction with acetone according to Scheme III is more important; hence with increase in the quantity of OH groups in acetylcellulose its solubility in acetone increases and its viscosity in solution falls. But with further increase in the number of the OH groups their interaction with one another (Scheme IV) develops strongly, and the solubility of the acetylcellulose once again deteriorates and its viscosity increases.

As a result of the opposite effects of Reactions III and IV, the solubility of acetylcellulose passes through a maximum and its viscosity through a minimum at about 56% acetyl group content.

3. When alcohol (and water) are added to acetone [6], the interaction of the solvent with the OH groups of the acetylcellulose increases because the molecules of the solvent, containing the polar OH groups solvate the OH groups of the acetylcellulose more strongly according to Scheme III. Hence, the addition of alcohols (or water) to acetone, while not changing in principle the basic scheme of interaction, displaces the maximum solubility and the minimum viscosity of acetylcellulose in solution to the right i.e., towards materials with a lower acetyl number. (The minimum viscosity found graphically corresponds to an acetylcellulose with 55% acetyl group content.)

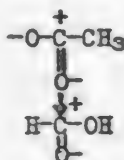
4. The dissolution of acetylcellulose in a mixture of dichlorethane and ethyl alcohol follows exactly the same course but to an even more marked degree, since neither of these liquids can dissolve acetylcellulose.

The molecule of dichlorethane, although it interacts with the acetyl groups of acetylcellulose according to Scheme I, nevertheless does so more weakly than does the molecule of methylene chloride, because of its larger size. Hence this interaction cannot oppose the interaction of acetyl groups according to Scheme IV, and when triacetylcellulose is treated with dichlorethane in the cold, only a swelling is usually observed, and no dissolution (acetylcellulose nevertheless dissolves in dichlorethane on heating because of a weakening of the intermolecular bonding according to Scheme IV).

The same things were observed in the treatment of secondary acetylcellulose with alcohol. The more OH groups there are in the material, the more they interact with alcohol or water according to Scheme II: but all the same under the usual conditions acetyl cellulose only swells and does not dissolve either in alcohols or in water, apparently because of the strong association of molecules of the HOR type [2]. But if dichlorethane is replaced by alcohol then at a definite ratio between the OH and OCOCH_3 group in the acetylcellulose, the dissolution of the macromolecules is not only possible but even very intense (specific viscosity of the solution very small).

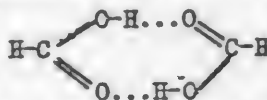
This can be explained by the facts that: 1) in this process both the OCOCH_3 and the OH groups of acetylcellulose react with solvent molecules and the interaction of macromolecules with themselves according to Scheme IV is less probable; and 2) in the mixture of dichlorethane/alcohol the association of the alcohol molecules is diminished and they commence to react in the more active monomeric form.

5. The interaction of acetylcellulose with 80% formic acid is somewhat different. This solvent brings acetylcelluloses of the most varied acetyl numbers into solution (from 49.9 - 61.4% acetyl group content); the intensity of the interaction of these substances with the solvents is approximately the same, since the specific viscosity of the solution of the different acetylcelluloses is the same. Thus, in solutions of different acetylcelluloses formic acid molecules solvate the OCOCH_3 and OH groups to practically the same extent. It is possible that this can be explained by the duplex character of the molecule



(V)

itself, since it has two types of polar group (CO and OH) and it can therefore react either with the OCOCH_3 groups of acetylcellulose according to the scheme



or with OH groups according to Scheme II. But this interaction is considerably weakened in both cases because, in concentrated aqueous solutions formic acid is strongly associated to the dimeric form, which reacts

6. On the basis of all these speculations we may suggest the possibility of the fractional separation of technical acetylcellulose into fractions differing in percentage of acetyl groups. Thus, for instance the addition of water or alcohol to an acetone solution of acetylcellulose improves the conditions for dissolving fractions containing a lower percentage of acetate groups, and worsens the conditions for dissolving fractions containing a high proportion of these groups. Hence the addition of water or alcohol to an acetone solution of acetylcellulose, other conditions being the same, should throw down a precipitate of acetylcellulose containing a high proportion of acetyl groups. Inversely, by adding to this acetone solution methylene chloride, or dichlorethane or other solvents which react only with the OCOCH_3 groups of acetylcellulose precipitate which should contain materials with a low acetyl number should be obtained.

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¹⁾ See Consultants Bureau English Translation, p. 819.

²⁾ See Consultants Bureau English Translation, p. 990.

MOLECULAR COMPOSITION OF CHLORINATED POLYVINYLCHLORIDE¹

B. E. Geller

The rapid development of the chemistry and physics of high molecular compounds has led to the production of a large number of new substances, having very valuable properties. Different types of polyvinylchloride are of great value in the production of fibers and films.

Produced and studied as early as 1912 by the Russian scientist Ostromyslen-sky [1] polyvinylchloride has drawn the attention of different branches of industry upon itself, thanks to its high chemical and bacterial stability, its favorable electrical insulating properties and the availability of its raw materials.

However, polyvinylchloride dissolves poorly in the usual solvents, which makes the production of film and fibers from its solutions difficult. It was found [2] that as a result of the further chlorination of polyvinylchloride, increasing its chlorine content from 56.5 to 63-65%, it became quite easily soluble in ketones, chlorinated hydrocarbons and other common solvents. The chlorination is performed, in tetrachlorethane [2] or chlorobenzene [3], with gaseous chlorine at 80-110°. The chlorinated polyvinylchloride (Pervinylchloride) obtained in this way has found wide application in the production of fibers, films, different covering materials, adhesives, etc., in the light, chemical and other industries [4], because it combines the properties of polyvinylchloride with an improved solubility. In spite of this, little work devoted to the study of the composition, structure and properties of pervinylchloride, has been reported.

The present work was directed to a study of the state of polymerization of industrial samples of the polymers and the preparation of chemically pure samples of pervinylchloride for further study.

EXPERIMENTAL²

To separate pervinylchloride into fractions we used two methods, fractional precipitation and fractional solution, of which the first method is already in use in industry.

Acetone, methylene chloride, chlorobenzene and dichloroethane were used as solvents and methanol, ethanol and butanol were used as precipitants.

In all cases the precipitates were gelatinous, but with repeated precipitations from acetone with methanol they became more compact, which was not observed with other combinations of solvents and precipitates. Hence, we used the combination of acetone and methanol.

It is known that in fractional precipitation, a small concentration of the high polymer in solutions facilitates the separation of the substance into a large number of fractions [5].

Previous experiments have shown that with an acetone solution whose concentration is greater than 10%, the viscosity is considerably increased and the

¹ Communication 1 dealing with the composition, structure and properties of chlorinated polyvinylchloride.

² In the experimental part of this work the laboratory workers V.G. Bulimov and K.N. Vanyushin participated.

uniformity of the precipitate is worse. Thus a 15% solution can only be divided into three fractions, while from a 10% solution six fractions can easily be obtained. We did not take the concentration below 10% because it was desired to operate with the largest weight fraction with the smallest possible volume of mixture.

The fractional precipitation was carried out as follows: a 10% solution of a technical sample of the polymer in anhydrous acetone, after previous filtration through two layers of muslin, and through a thick copper gauze in a steel tube was introduced into a tared wide-mouthed flask, taking precautions against loss of acetone by evaporation. After withdrawing the sample for determining the concentration, the solution was weighed and the quantity of polymer dissolved in it was determined. A mixer, and the end of a dropping funnel, were inserted into the flask and the apparatus was tested for leaks.

The experiments were carried out at room temperature (18-20°). The precipitation of a given fraction was taken as complete when a stable turbidity appeared.

The rate of addition of methanol was adjusted so that the time from beginning to end of the precipitation of the fraction was not more than four hours. After the end of precipitation the solution was stirred for a further one hour.

The gelatinous precipitate was allowed to stand for 12-18 hours and was then carefully decanted.

The fraction for repeated precipitation was dissolved in the smallest possible quantity of acetone, and the solution was gradually added through the dropping funnel to methanol which was being stirred. The ratio of acetone to methanol after the repeated precipitation was 1:3 (by volume). As a result of the reprecipitation a white flocculent or powdery precipitate was obtained.

After standing, the mixture was decanted and the precipitate was quantitatively transferred to a tared porcelain basin, and dried to constant weight at 80°. The decanted liquor was evaporated to dryness on a water bath. The weight of this residue was added to the weight of the main part of the fraction.

The precipitation of the succeeding fractions was made in a similar manner, and was terminated when the ratio of methanol to acetone in solution was 1:3 (by volume). After this the decanted liquor was evaporated, as a result of which there was obtained a later fraction in the form of a resinous brown residue, having an unpleasant smell.

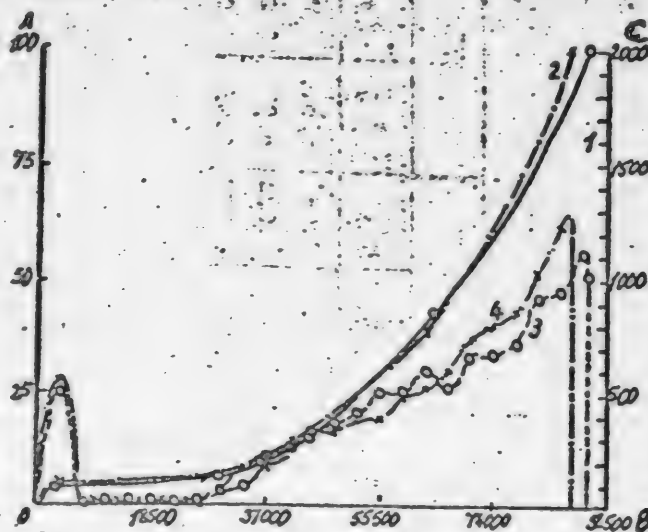
Technical samples of the polymer were divided into six fractions. To determine the molecular weight, the specific viscosity of an 0.2% (by volume) solution of pervinylchloride in chlorobenzene was determined. The degree of polymerization was calculated from Staudinger's equation in which K_{equiv} was taken as 1.10^{-4} [5].

Since in the extended chlorination of polyvinylchloride one atom of chlorine was added for each 3 vinylchloride units; the average molecular weight of the unit was 74.

To confirm the reproducibility of the results, the fractionation of one sample of polymer was repeated by fractional precipitation. The data in the Table show that the method described above gives reproducible results.

For the separation of pervinylchloride into fractions we also employed fractional solution in the same system (acetone/methanol). The ratio of the components of the solvent mixture was chosen to be the same as in fractional precipitation. The modulus of the dissolved mixture was 25. The time of solution of one fraction was 4 hours. In other details the method was similar to that described above.

For graphical representation of the state of polymerization of the product, integral curves were constructed directly from the experimental points and afterwards, by graphical differentiation, differential curves of distribution were obtained.



Integral and differential distribution curves of molecular weight for two methods of fractionation.

A - yield of fraction (in %); B - molecular weight;
C - ratio $\frac{\Delta\phi}{\Delta\eta_m}$ (scale 1/5).

1 - integral curve of precipitation; 2 - integral curve of solution; 3 - differential curve of precipitation; 4 - differential curve of solution.

In the Fig. are set out the results of fractionating one of the samples of polymer by the two methods, calculated on 100% yield.

The differential distribution curves show that technical samples of pervinylchloride consist basically of two parts, one having a low molecular weight of up to 5000, and one having a high molecular weight more than 25,000. A considerable number of industrial samples of pervinylchloride were examined and it was found that the character of the distribution was in all cases the same.

In order to make a more detailed study of the chemical composition, the chlorine content in each fraction was determined by the method which we worked out earlier [6]. In addition, the total ash and iron contents of the fractions were determined, (the iron colorimetrically).

The data of Table 2 show that, apart from the difference in molecular weight between Fractions I-V and VI, they differ in chemical composition: the low molecular fraction is a complicated mixture of chlorinated aromatic compounds formed in the polymer after precipitation, in the process of production.

The difference between the two heterogeneous parts which has been established suggests a method for the removal of the considerable deficiencies of pervinylchloride and of articles composed of it: the unpleasant smell and the iron compounds causing, as is known, a catalytic depolymerization of the polyvinyl polymer. One of these is to render the conditions of chlorination milder in order to avoid various side reactions. This diminishes the quantity of

TABLE I

Fractionation of the residue of benzene precipitation

Exp. No.	Yield (in g.)	Sol. concn. (in g./100 g.)	Yield of fraction (in g.)					Total yield		Loss (in g.)
			I	II	III	IV	V	VI	(in g.)	
1	331.79	0.91	23.5001	6.7186	1.8782	0.6506	0.4246	2.0158	34.6879	1.4762
2	342.27	0.50	22.7492	6.4742	1.5010	0.5424	0.4722	2.0594	33.5773	2.0413
3	329.77	0.63	34.4132	5.9949	1.4217	0.4922	0.5010	2.0374	33.8474	1.5012

Characterization of fractions

Expt. No.	I		II		III		IV		V		VI	
	Yield (in g.)	η_{sp}	Yield (in g.)	η_{sp}	Yield (in g.)	η_{sp}	Yield (in g.)	η_{sp}	Yield (in g.)	η_{sp}	Yield (in g.)	η_{sp}
1	67.74	0.240	19.37	0.148	3.99	0.122	1.07	0.107	1.22	0.061	5.81	0.010
2	67.17	0.228	19.35	0.171	4.43	0.141	1.59	0.112	1.39	0.084	6.07	0.008
3	59.17	0.232	17.74	0.157	4.20	0.128	1.46	0.109	1.47	0.077	5.96	0.009

impurities in the polymer and improves its quality. On the other hand the separation of the middle fractions ensures the preparation of pure ashless samples, for the study of the chemical and physico-chemical properties of pervinylchloride.

SUMMARY

1. The non-homogeneity in composition of industrial samples of pervinylchloride polymers has been demonstrated.
2. It has been shown that the main part of the different foreign impurities is in the low molecular fractions, not present in the polyvinylchloride from which it was derived.

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RHEOLOGICAL PROPERTIES OF VINYLALKYL ETHER POLYMERS

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There are references to the rheological properties of the polymers of simple vinyl ethers only in the patent literature [1]. At present a large number of different polyvinylalkyl ethers have been synthesized, which enables a comparison to be made, particularly of polymers which contain normal and iso-alkoxy groups.

In the USSR an extremely simple method of synthesizing vinyl ethers has been worked out by Favorsky and Shostakovsky [2]. According to this method simple vinyl ethers are obtained by interaction of acetylene with alcohol and phenol as follows:



The existence of a sufficient number of ethers and of a rich assortment of the corresponding polymers permitted us to make a study of the rheological properties of these polymers in mineral oils. The investigation showed that their viscosity is strongly dependent on their character and structure. The chain length of the polymer and its degree of branching has a considerable influence on its rheological properties. Extremely important also is the connection between the structure of the polymer and its solubility in hydrocarbons.

EXPERIMENTAL

Polymers of vinyl-n-butyl ether. For the preparation of the polymer, vinyl-butyl ether obtained according to the method of Favorsky and Shostakovsky was polymerized in the presence of ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as a catalyst [3].

The ether used for polymerization should be purified from admixed butyl alcohol and other contaminants. For this purpose it is repeatedly washed with water, dried over potash or other alkali drying agent and then distilled. For polymerization the fraction boiling at $93 - 94^\circ$ was taken, having the following constants: specific gravity $D_4^{20} = 0.7795$; refractive index $n_D^{20} = 1.4010$; viscosity (Ostwald) at 20° $\eta = 0.4326$ centipoises.

The polymer obtained is a light yellow, very viscous resin. The product dissolves quite well in benzene and lubricating oil, even in the cold, on simple mixing. The solution in oil is completely stable and shows no tendency to separate on standing.

The constants of the polymer are as follows: Density $D_4^{20} 0.932$; refractive index $n_D^{20} 1.4588$. The viscosity of an 0.1 M benzene solution, the concentration being calculated on the initial molecule, and the viscosity being measured at 20° by the Ostwald method, was 0.8722 centipoises and, expressed as a ratio to the viscosity of benzene, 1.35. The molecular weight of the polymer was determined cryoscopically in benzene, and showed the degree of polymerization to be 30 - 40. The flash point was determined by the Brenken method and found to be $208-210^\circ$.

Since the polymer is not a standard product we devoted some time to determining its constants.

The polymer obtained may be contaminated with the monomer and with the reprecipitating solvent. The flash point and viscosity are quite considerably changed by the presence of the monomer. Data relative to the change of these constants are set forth in Table 1.

TABLE 1

Constants of a Mixture of Polymer with the Original Ether.

Composition of mixture	Density	Refractive index	Viscosity of 0.1 M solution at 20°		Flash point (Brenken)
			Absolute (in centipoises)	Relative (to benzene)	
Pure polymer ...	0.9321	1.4588	0.8722	1.35	212°
90% polymer + 10% ether...	0.9028	1.4540	0.8442	1.31	180
75% polymer ... + 25% ether...	0.8979	1.4463	0.8211	1.25	140
50% polymer ... + 50% ether...	0.8528	1.4308	0.7450	1.15	-
25% polymer ... + 75% ether...	0.8160	1.4160	0.6918	1.07	-

Table 1 shows that the flash point, and in particular the viscosity of the benzene solution, can be used as indexes of the purity of the polymer. The change of the viscosity is almost directly proportional to the concentration of polymer in monomer.

The polymer dissolves extremely well in mineral oils. Even at small concentrations of polymer the viscosity of the oil is greatly increased. The viscosity temperature curve is also improved (viscosity index). The results obtained in the determination of the viscosity and of the viscosity indexes of different samples of oil are given in Table 2.

As can be seen from this table, addition of only 5% of polymer to a machine mineral oil converts this oil to the class of a winter aviation oil, having a good ratio of viscosities at 50 and 100°. The action of the polymer is more effective than addition of "paraton" [4]. The details can be seen at a glance from Table 3.

Additions of different quantities of polymer and of paraton to machine oil raise the viscosity index to 120, i.e., by 50 units, in the first case and to 85, i.e., by only 15 units, in the second case.

That the polymer improves the viscosity temperature curve of the oil to a larger degree than paraton is also evident from a comparison of the corresponding values for Autol-10 with 5% addition of polymer or 10% of paraton. At 100° both samples had approximately the same viscosity, but the viscosity index with the polymer was 90 and with paraton 77.

It is extremely interesting to note that the raising of the viscosity of an oil and the improvement of its viscosity index depend strongly on the degree of polymerization of the sample. Thus, for example, the polymer of vinyl-n-butyl ether with a lower degree of polymerization was investigated. The results are set out below.

The sample had the following characteristics; refractive index n_D^{20} 1.4564, density D_4^{20} 0.9274, viscosity of 0.1 M benzene solution 0.7237 centipoises, molecular weight in benzene 2170, flash point (Brenken) 210°.

TABLE 2

Change of Viscosity Indexes of Oils on Addition of Polymer

Sample of oil	Viscosity, Engler		Kinematic viscosity (in stokes)		Viscosity index (Din and Davis)
	50°C	100°C	50°C	100°C	
Machine lubricating oil	6.25	1.65	0.468	0.0852	70
ditto + 5% polymer	9.90	2.27	0.743	0.146	120
ditto + 10% polymer	16.50	2.90	1.253	0.218	120
Autol	9.72	1.89	0.736	0.106	40
ditto + 5% polymer	16.13	2.62	1.233	0.178	90
Aviation oil SO	21.12	2.88	1.602	0.207	81
ditto + 1% polymer	23.10	3.10	1.745	0.223	86
ditto + 3% polymer	26.40	3.58	2.020	0.262	96
Spindle oil (light machine oil)	2.06	1.25	0.124	0.034	-
ditto + 10% polymer	5.73	1.95	0.431	0.112	-

TABLE 3

Comparison of the Effects of the Polymer and Paraton on the Viscosity of oils

Sample of oil	Viscosity, Enger		Kinematic viscosity (in stokes)		Viscosity index (Din and Davis)
	50°C	100°C	50°C	100°C	
Machine oil	6.25	1.65	0.468	0.0852	70
ditto + 5% polymer	19.90	2.27	0.748	0.146	120
ditto + 5% paraton	9.32	2.0	0.706	0.118	85
Autol-10	9.72	1.89	0.736	0.106	40
Autol-10 + 5% polymer	16.13	2.62	1.233	0.178	90
ditto + 5% paraton	14.0	2.24	1.02	0.136	55
ditto + 10% paraton	18.0	2.72	1.32	0.175	77

TABLE 4

Change of Viscosity of Machine Oil by Addition of Different Quantities of Polymer¹

Sample of oil	viscosity, Enger		Kinematic viscosity (in stokes)		Viscosity index (Din and Davis)
	50°C	100°C	50°C	100°C	
Lubricating oil	6.25	1.65	0.468	0.085	70
ditto + 4% polymer	8.51	1.91	0.645	0.12	80
ditto + 5% polymer	9.34	1.99	0.707	0.116	83
ditto + 8% polymer	11.48	2.27	0.869	0.146	100
ditto + 10% polymer	13.07	2.45	0.990	0.162	102
Polymer	-	98.9	-	7.493	-

¹) Data obtained by T.N.Tikholaz.

The effects of the sample of polymer on lubricating machine oil were investigated. The results obtained for solutions containing different quantities of polymer are set out in Table 4.

As can be seen from Table 4 the substance with lower molecular weight must be added in larger quantities to attain the viscosity given by substances with a molecular weight of about 4000. The viscosity of the oil increases almost proportionately to the quantity added. This correlation is correct at 50°, as well as at + 100° (Fig. 1).

TABLE 5

Effect of Polymer No.2 on Wear in the Presence of Turbine Oil

Nature of oil	Turbine oil	Turbine oil + 2% polymer No.2	Turbine oil + polymer (experimental batch)
Width of track (in μ)	96	46	32

TABLE 6

Effect of the Polymer of Vinyloctyl Ether on Properties of Oils

Sample of oil	Viscosity Engler		Viscosity index	Setting point
	50°C	100°C		
Autol-10	12.36	2.06	41	-13°
ditto + 4% vinyl polymer	21.04	3.08	90	-13
Aviation oil SO	23.04	3.05	75	-17
ditto + 4% vinyl polymer	33.26	4.34	102	-16

The effect of additions of polymer on the setting point of the oil was also investigated. It was found that the introduction of high viscosity additions did not affect the setting point but in individual cases even lowered it.

Effect of vinyl polymer on oiliness. Under the conditions of semi-fluidity and boundary friction, in contrast to friction with complete lubrication of fluidity, the viscosity and the viscosity temperature relations do not determine the lubricating action of the oil. This action depends on the so-called oiliness. The oiliness comes into play completely when the lubricating film is so thin that its volumetric mechanical property (viscosity) recedes into the background.

Thus, to estimate the oiliness it is necessary to examine the lubricating action in thin (boundary) oil films. To obtain a quantitative measure of the oiliness the so-called quantitative index of lubricating effectiveness in these conditions must be measured.

The determination of this index and the method of its measurement are involved in the basic problem of the evaluation of oiliness.

The solution of this problem is complicated by the insufficiency with which the phenomena of boundary lubrication has been studied, and also by their great complexity.

Investigations of this important practical problem in the Laboratory of Thin Layers of the Institute of Physical Chemistry of the USSR Academy of Sciences (Director Prof. Deryagin) have made it possible, however, to give an extremely simple and methodical relation, and a solution of the problem of evaluating oiliness which is in accordance with practical findings.

The bases of this index are two: First, the so-called "life" of the lubricating film measured by the time τ , in which a thin lubricating film of given thickness (order 0.1 - 1.0 μ) can maintain its lubricating action under the conditions of boundary friction. The end of the lubricating period is observed as that at which the friction jumps to the dry friction level.

(More detailed bases of this method have been published earlier [5]). The second index is the wear of one of the friction surfaces, obtained by determination of the wear on a sample in the presence of a given sample of oil.

To obtain these two complementary indexes, of lubricating capacity or oiliness, a specially simple DL apparatus constructed by Deryagin and Lazarev has recently been constructed. In this apparatus a frictional pair is formed by a steel cylinder turning around a horizontal axis (1440 rpm) and a stainless steel wire, the horizontal part of which is attached to a dynamometer, and the vertical part is tensioned by a weight. The wire is in contact with a quadrant of the cylinder surface. The total frictional drag is measured as the increase of the reading on the dynamometer. As a measure of the wear of the metal the width of the track produced by wear for 10-minutes under a weight of 2kg is taken. During the period of wear an excess of oil (thickness about 1 mm) is fed around the wire. Inversely, to determine the "life", the film of oil is fed on to the cylinder in the form of a layer of thickness about 0.23μ , by a special method proposed by Deryagin.

Besides this, initially, the life of the film is determined in an apparatus with plane frictional surfaces. (disc and flat sliding block). The observations on the life of the oil film are conveniently represented graphically, plotting time from the beginning of wear on the abscissa and the coefficient of friction on the ordinate. Detailed tribograms clearly indicate the kinetics of "wear" of the oil film, leading up to its breakdown to dry friction.

Measurements with the plane frictional surfaces have been carried out by Kusakov, Zakhavaeva and Lazarev.

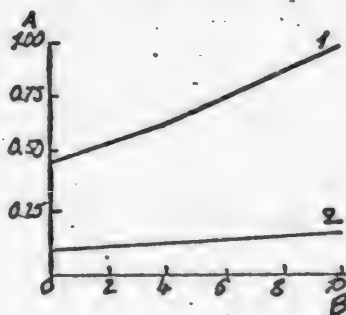


Fig. 1. Change of viscosity of machine oil, pure and containing polymer. A - Kinematic viscosity (in stokes); B - % polymer. Temperature in $^{\circ}$ from -50 to $+100$. 1 - Oil + polymer; 2 - pure oil.

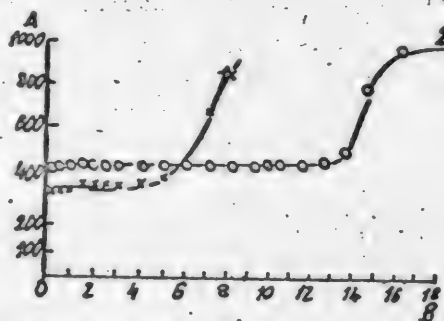


Fig. 2. Wear resistance of a film of turbine oil. A - Friction (in g); B - time (in minutes). 1 - Turbine oil; 2 - ditto + 2% polymer.

The following samples of vinyl polymers were studied.

Sample No.1, polymer of vinyl-n-butyl ether treated to remove low molecular products with sulfuric ether and by precipitation of the polymer from a solution in ethyl alcohol; constants: refractive index n_D^{20} 1.4574; density D_4^{20} 0.9290; viscosity of 1% benzene solution at 20° 0.8411; molecular weight, determined cryoscopically in benzene 3170.

Sample No.2. The same sample, but subjected to a second precipitation; constants: n_D^{20} 1.4583, D_4^{20} 0.9302; viscosity of benzene solution 0.8582; mol. weight 4220.

Sample No.3, was a polymer of vinyl-n-butyl ether precipitated by driving off the low molecular weight products in vacuum at 100 - 120°, constants: n_D^{20} 1.4570 D_4^{20} 0.9321, viscosity of 1% benzene solution 0.8119, molecular weight 2240.

Sample No.4. Polymer of vinyl-isobutyl ether, prepared by Sidelkovskaya by polymerization of the vinyl-isobutyl ether with solid SnCl_2 as a catalyst; after re-precipitation from ethereal solution with ethyl alcohol the polymer had a refractive index n_D^{20} 1.4518 and a molecular weight (in benzene) of 2250.

The results of the observations by Zakhavaeva of the "life" or wear resistance of films of turbine oil using plane friction surfaces are shown graphically in the form of tribograms in Fig. 2. The tension on the wire was provided by a weight of 500 g., the thickness of the film was 1μ .

The conditions of experiment were the following. The load on each of the two sliding blocks was 1200 g, the area of each about 1 cm^2 . The rate of rotation (of the disc) was 150 cm/sec. The thickness of the film was 0.02μ , concentration of polymer 2%. In Fig. 3. are shown results obtained under similar conditions illustrating the effect of addition of 2% Polymer No.3 to gun oil.

It should be noted that each experiment was stopped when a coefficient of friction of 0.5 was obtained, i.e. before dry friction, corresponding to a coefficient of friction of about 0.7 was reached in order to avoid the deterioration of the surface associated with dry friction.

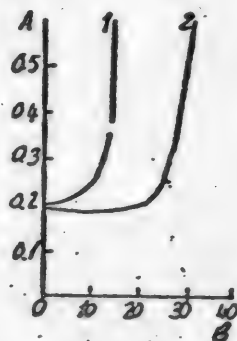


Fig. 3. Tribogram of a film of gun oil, pure and with additions of polymer. A - Coefficient of friction; B - time (in minutes). 1 - Pure oil; 2 - ditto + 2% polymer.

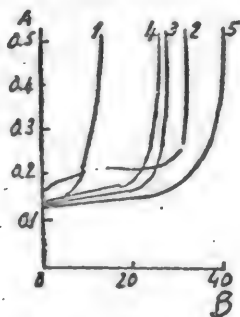


Fig. 4. Tribograms of turbine oil, pure and with additions. A - Coefficient of friction; B - time (in minutes). Load on sliding block 1200 g; rate of rotation of the disc 150 cm/sec; thickness of layer 0.01μ . 1 - Pure turbine oil; 2 - ditto + 2% Sample 1; 3 - ditto + 2% Sample 2; 4 - ditto + 2% Sample 3; 5 - ditto + 2% Sample 4.

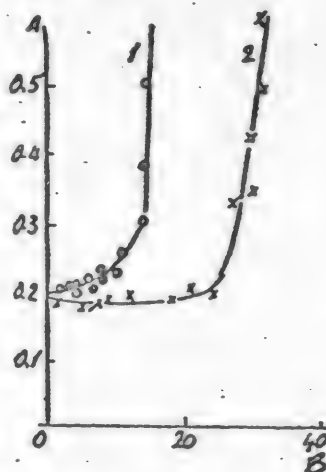


Fig. 5. Tribograms of films of pure gun oil with and without additions. A - Coefficient of friction; B - time (in minutes). 1 - Pure gun oil; 2 - ditto + 2% Sample 3. Conditions of experiment the same as for Fig. 4.

As can be seen from the graphs presented, all the samples investigated raise the life of films of turbine oil and consequently improve its lubricating capacity. It should be noted that the lower molecular weight polymer of normal butyl vinyl ether has smaller effect than the more highly polymerized substance. At the same time, apparently, the oiliness depends strongly on the structure of the initial ether, in particular on the branching of its chains. Thus, the polymer of vinyl isobutyl ether (Sample No.4) although its degree of polymerization was less, nevertheless caused a maximum increase in oiliness.

The tribograms in Fig. 4 were obtained with the wire apparatus under the following conditions; diameter of the working cylinder 4 cm, diameter of wire 0.27 mm, load on the wire 0.5 kg, rate of rotation of the pulley 1440 rpm. These data reveal that in these conditions of considerably larger specific load the increase of life in the film of turbine oil on addition of polymer was no less.

One of the most important indexes of oiliness which is at the present time very widely used in practice is the diminution in wear caused by lubrication.

The data given in Table 5 indicates the positive effect of Polymer No.2 on the wear in the presence of turbine oil as a lubricant. Experiments were carried out on the wire apparatus DL, which permits the estimation of the wear from the width of the cylinder track. The load on the wire was 2 kg, the time of wear 10 minutes. The diameter of the roller was 2 cm (Fig. 5).

Thus, these results clearly indicate the effect of vinyl polymer on the diminution of the wear of metals.

Polymer of vinyl octyl ether. Laboratory examination of this substance showed it to have valuable properties: it is apparently even better than the other polymers. Only limited quantitative experiments were made on it, which, however, gave extremely interesting results, shown in Table 6.

SUMMARY

1. It has been shown that the polymers of vinyl alkyl ethers greatly improve the viscosity temperature curve (i.e., viscosity indexes).
2. A considerable diminution of the wear of metals in the presence of 2% solution of vinyl alkyl ether polymers has been demonstrated.

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SYNTHESIS OF 3-METHYL-4-ETHYLTHIOPHENE

I.Ya.Postovsky, H.P.Bednyagina and V.F.Kuznetsova

The properties of alkylated thiophenes have been little studied and this makes the identification of such thiophenes difficult, when they are separated from petroleum distillates.

It was of special interest to us, in view of the opinion we have expressed earlier about the connection between the structure of the so-called thiophenogenes and porphyrins, to discover in petroleum distillates, 3-methyl 4-ethylthiophene (analog of opsopyrrol, ethyl methyl pyrrol) having an arrangement of the methyl and ethyl radicals characteristic of porphyrin.

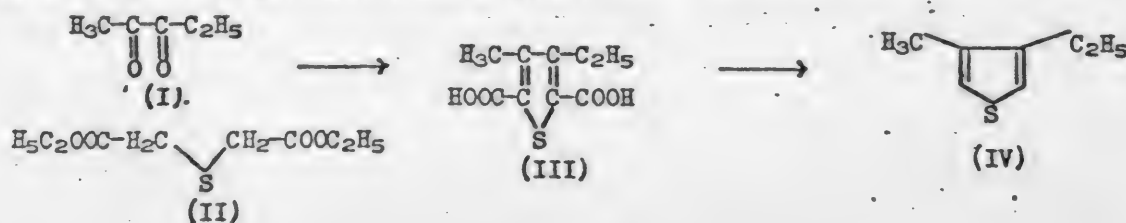
In a study of samples of petroleum from the Urals containing a high quantity of sulfur compounds (Chusov, Ishimbaevsk, Krasnokamsk) we showed [1] that thiophene compounds, giving the indophenine reaction, are not contained as such in the petroleum but are formed in distillation.

In our experiments asphaltenes were precipitated from samples of these petroleum with petroleum ether, and the filtrate was chromatographed on silica gel. From the silica gel a colorless oil was extracted, a highly viscous "heavy oil" with a slight smell of turpentine (6 - 8% on the petroleum) and a mobile "light oil" with a kerosene smell (70 - 75% on the petroleum). This "light oil", separating in the cold, did not give the indophenine reaction characteristic for thiophene. Only on distillation of the light and heavy oils at 150-250° could a positive reaction for thiophene be quite definitely obtained in the distillates. It was shown earlier that in all probability the thiophene compound formed in the distillation of the samples investigated does not arise from a synthesis, but from a breakdown of some complex but labile sulfur compounds, called by us provisionally "thiophenogenes" [1].

We further observed that in the distillate oils, obtained chromatographically from the samples of sulfur-containing petroleum which we investigated, and in a number of bitumens, as a rule the indophenine reaction appeared only in those cases where the original products (petroleum, bitumen) did not contain porphyrin. From this we were able to deduce a possible connection between the structure of "thiophenogenes" and porphyrins. Porphyrins can, in the process of petroleum formation, be converted to heterocyclic compounds (Yurev) to give the sulfur containing heterocyclic compounds "thiophenogenes" [1].

3-Methyl-4-ethylthiophene, as far as can be judged from the literature, has not been described. Hence we proceeded to synthesize it. Such a methyl-ethylthiophene, with 3 α -positions, may be of interest for the preparation of di- or polythiophenyl methane, a model of the thiophene compounds which are unstable on heating.

The initial substance for the synthesis of 3-methyl-4-ethylthiophene was pentanedione-2,3 (I), which was condensed with thiodiglycolic ester (II) giving the dicarboxylic acid (III) and the latter on decarboxylation was converted to 3-methyl-4-ethylthiophene (IV):



The method for synthesis of substituted thiophenes proposed by Ginsberg [2] for obtaining phenylated thiophenes was selected. Unsymmetrical β, β' -disubstituted thiophenes have so far not been synthesized, but there is no doubt that the synthesis of this and other unsymmetrically substituted thiophenes can be carried out by this method.

The 3-methyl-4-ethylthiophene obtained gives the indophenine reaction and forms a complex with mercuric acetate. In the pure form it has a characteristic pleasant aromatic odor. It boils at 165-166° and, as would be expected, this b.p. agrees with the b.p. of the corresponding aromatic hydrocarbon o-methylethylbenzene (165°).

TABLE

Physical Constants of Methyl-Ethylthiophenes.

Position of groups in methyl-ethylthiophenes		B.p. (in °)	d_4^{20}	Literature
methyl	ethyl			
2-	3-	156-7	-	[3]
3-	2-	160-161.5	-	[3]
2-	5-	159.8-160.4	0.9663	[4]
2-	4-	162-164	0.9742	[4]
4-	2-	-	-	Not described
3-	4-	165-166	0.9976	

As can be seen from the Table, 3-methyl-4-ethylthiophene has the highest b.p. and density of all the methyl-ethylthiophenes described in the literature.

EXPERIMENTAL

3-Methyl-4-ethyl-2,5-thiophenedicarboxylic acid. 15 g of sodium was dissolved in 300 ml of absolute alcohol, with strong cooling, and to this solution of sodium ethylate was added a mixture of 30 g thiodiglycolic ether (with a b.p. of 259 - 260° [5]) and 20 g of pentanedione-2,3 (with a b.p. of 108° [6]). The brown reaction mixture was left to stand for 2 hours at a temperature of 0-5°. Afterwards, water was added to the mixture to dissolve the precipitate. The excess alcohol was distilled off, and the mixtures were acidified with HCl. On standing, flocculent thiophenedicarboxylic acid separated out. The product was filtered off and dried in a dessicator. The yield was 7.5 g, i.e. 20% of theory. The microcrystalline powder was yellow or light brown. It did not have a definite melting point, but on heating gradually darkened and decomposed. The product was converted to thiophene without purification.

3-Methyl-4-ethylthiophene. 20 g of 3-methyl-4-ethyl-2,5-thiophenedicarboxylic acid was dissolved with 20 g of soda lime, heated with a flame in a small retort or a bent test tube, as a result of which a yellow oily liquid and water distilled off. The liquid was separated from the water, dried over a calcium chloride and redistilled. After double redistillation through a fractionating column, 7 g (62% of theory) of substance with a b.p. of 165-166° was obtained.

d_4^{20} 0.9976;

n_D^{20} 1.5186

γ^{20} 1.24

Found: MR 39.26; P 307.7

$C_7H_{10}S$. Calculated: MR 39.39; P 308

0.1237 g substance: 14.630 g benzene; Δt 0.345°.

Found: M 125.0

$C_7H_{10}S$. Calculated: M 126.
0.1080 g substance: 0.2016 g $BaSO_4$.
0.1085 g substance: 0.2052 g $BaSO_4$.
Found % : S 25.63, 25.87
 $C_6H_{10}S$. Calculated %: S 25.57.

Mercuric acetate complex of 3-methyl-4-ethylthiophene. 3-Methyl-4-ethylthiophene was added dropwise to an aqueous solution of mercuric acetate. The mixture was boiled for a few minutes, after which a white curdy precipitate of the mercuric acetate complex came down. The precipitate was filtered off, carefully washed with water and afterwards re-crystallized from acetic acid.

0.1023 g substance: 0.0366 g $BaSO_4$
Found % : S 4.89
 $C_4S(CH_3)(C_2H_5)(CH_3COOHg)_2$. Calculated %: S 4.96

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ANALYSIS OF THE COPOLYMERS OF METHYL METHACRYLATE
AND ALLYL METHACRYLATE¹⁾

B. N. Rutovsky and A. M. Shur

The direct analysis of methyl and allyl methacrylate copolymers is beset by a number of difficulties, because of their similarity in chemical properties. While the original monomers differ in degree of unsaturation, this difference is practically absent in the polymerization products. Hence it is impossible to analyze a copolymer by determination of the bromine number. Determination of the alkoxyl numbers, following Zeisel and others, though it has found some application for the investigation of styrene and methylmethacrylate copolymers [1] and of cellulose and starch ethers [2], has the inconvenience that hydriodic acid can act on the copolymer methyl and allyl methacrylates, forming, beside methyl iodide, allyl iodide or its derivatives.

The methods described in the literature for the analysis of copolymers, based on the determination of their content of an element (chlorine [3], nitrogen [4], etc.), present in one of the monomers but not present in the other (for example in the copolymer of vinyl chloride and methyl methacrylate), is likewise inapplicable here.

The determination of copolymer by the characteristics of the functional groups in one of the monomers or by elementary composition, can likewise not be applied, since both methyl and allyl methacrylates are esters and do not differ sufficiently in elementary composition. Mayo and Leuris [5] used the analysis of the elementary composition for investigating the copolymers of styrene and methyl methacrylate, in which the difference in hydrogen content between the pure polystyrene and the pure polymethylmethacrylate is $92.22 - 59.72 = 32.50\%$. The difference in hydrogen content between methyl and allyl methacrylates is only $66.66 - 60 = 6.66\%$, while the difference in oxygen content is $32 - 25.39 = 6.61\%$, and the hydrogen content in the two monomers is practically identical, within the limits of accuracy of analysis (8 and 7.94%). If to this is added the fact that a small error in the determination of the hydrogen content leads to a large error in the determination of the copolymer composition, even when the difference in hydrogen contents is relatively large, it becomes clear that the use of such a method for the analysis of our copolymers would lead to extremely inaccurate results.

¹⁾ Communication II dealing with the copolymerization of methyl methacrylate with esters of unsaturated alcohols and methacrylic acid.

All these considerations decided us against direct analysis of the copolymer, and led us to develop a method in which the copolymer itself was not analyzed but the mixture of unreacted monomers. Comparison of the results of analyzing this mixture and the mixture of the initial monomers provides a basis for calculating the composition of the copolymer.

EXPERIMENTAL

Separation of the mixture of monomers from the polymer. After carrying the polymerization to the desired stage, the process was stopped by rapid cooling, and the mixture of monomers distilled off under a pressure of about 1-2 mm Hg at room temperature. For extracting the last traces of monomers, the temperature at the end of the process was taken up at first to 100° and then to 150°. Confirmatory experiments with a solution of the copolymer in the monomers, in the presence of benzoyl peroxide, showed that under these conditions the monomers distil off practically quantitatively and do not polymerize further. The distillation was taken as finished when the weight of monomer did not vary in the third place between two successive weighings.

The distilled monomers were condensed in a U-tube immersed in liquid air, from whence they were transferred quantitatively to a flask for analysis.

Analysis of the mixture of monomers by bromine number. Since the bromine numbers of methyl and allyl methacrylates differ considerably from one another (the theoretical figures are 159.6 and 263), the bromine number of the monomer mixture can serve as the basis for determination of the initial and final ratio of the monomers, and consequently of the composition of the copolymer.

To decide the accuracy of different methods of determining bromine numbers, a series of comparative analyses were carried out with one and the same sample of methyl methacrylate, freshly distilled at 99-100°. The analyses were made with a bromide-bromate solution and with solutions of bromine in chloroform.

Apart from this, analyses were made with solutions of bromine in chlorobenzene. This method was of interest since chlorobenzene is less volatile than chloroform, and the rate of addition of bromine to allyl benzoate is somewhat greater for chlorobenzene than for chloroform [6].

For the bromide-bromate method, the usual bromide-bromate solution was used [7], containing 5.568 g of potassium bromate and 40 g of potassium bromide per liter of solution. The chloroform solution contained 44.5 g of bromine and the chlorobenzene solution 76.5 g bromine/liter. After adding the bromine solution to the weighed monomer (in the bromide-bromate method), 1 ml of strong HCl was added for every 25 ml bromide-bromate solution, the mixture was stood in the dark for 12 hours, after which a solution of potassium iodide was introduced and the mixture was titrated with thiosulfate (titer = 0.0427).

The analytical results are set forth in Table 1.

Results nearest to the truth were obtained, as can be seen from Table 1,

in Experiments Nos. 7 and 8 with chlorobenzene solution; but with increase in the weight (Experiments Nos. 9 and 10) the bromine number was considerably lowered. Increase in the time of standing, from 12 to 24 hours (Experiments Nos. 11 and 12) did not improve the results. In all cases (excluding Experiments Nos. 1, 7 and 8) the deviation of the bromine numbers from the theoretical was large and the reproducibility was unsatisfactory.

TABLE 1

Results of the Determination of Bromine Numbers of Methyl Methacrylate by Different Methods

Expt. No.	Method of analysis	Weight of monomer (in g)	Bromine number
1	Bromide-bromate.....	0.673	154
2	Bromide-bromate.....	0.603	150
3	Bromide-bromate.....	0.535	151.5
4	Bromide-bromate.....	0.564	150
5	Bromine in chloroform.....	0.498	121
6	Bromine in chloroform.....	0.561	124
7	Bromine in chlorobenzene.....	0.515	155.5
8	Bromine in chlorobenzene.....	0.521	156
9	Bromine in chlorobenzene.....	1.006	149
10	Bromine in chlorobenzene.....	0.030	148
11	Bromine in chlorobenzene.....	0.869	145
12	Bromine in chlorobenzene.....	0.870	145

A check of the chlorobenzene method on the given mixture of monomers also gave large deviations. Thus, analysis of a mixture of monomers by direct determination of bromine numbers appears useless.

Analysis of the mixture of monomers by saponification number. Attempts to analyze the mixture of monomers by determining the saponification number of the mixture likewise gave unsatisfactory results. The divergences were of the order of 10%, relative to the quantity of monomers taken.

Analysis of the mixture of monomers by determination of the allyl alcohol, obtained by saponification of allyl methacrylate. Allyl alcohol, in distinction from allyl esters, adds bromine very rapidly. Therefore there is no need for the extended period of interaction after addition of bromide-bromate solution; the titration may be made even 1 minute after its addition. With such a short period of interaction all danger of bromination disappears. This method of determining allyl alcohol is very accurate. Hatch and Estes [8] report that the error in the determination of allyl alcohol in this manner does not exceed 0.07%. For the mixture of allyl and methyl methacrylates this method is made more convenient by the fact that the bromine number of a single substance and not of a mixture is determined, which considerably increases the analytical accuracy.

The mixture of methyl and allyl methacrylates was analyzed as follows: a weighed quantity of the monomer of the given composition was boiled with an excess of alcoholic alkali (titer 0.0353) for two hours under reflux. The mixture was diluted with an equal volume of water and the alcohol, formed in saponification, was distilled off together with the water. The distillation was carried on until a dry residue was formed in the flask. To decrease the loss of allyl alcohol in the receiver, 25 ml of distilled water was added before distillation and the receiver was cooled with water as well. Control experiments

showed that cooling with ice was unnecessary. Allyl alcohol in the distillate was determined by the bromide-bromate method and was calculated as allyl methacrylate.

The results of some typical analyses are given in Table 2.

As can be seen the deviations between the quantities of monomer quoted are not large and are quite acceptable.

TABLE 2
Results of Analysis of a Mixture of Monomers by Determination of Allyl Alcohol

Composition of the given mixture		Allyl methacrylate (in g)		Methyl methacrylate found from saponification number	
Allyl methacrylate (in g)	Methyl methacrylate (in g)	(in g)	(% deviation)	(in g)	(% deviation)
0.312	0.649	0.310	-0.64	0.538	-17.1
0.509	0.919	0.501	-1.57	0.833	-9.35
0.635	0.435	0.430	-0.7	-	-

Simultaneous with the determination of the allyl methacrylate, we attempted to determine the quantity of methyl methacrylate from the consumption of alkali in the saponification of the mixture. For this the dry residue, remaining in the flask after distillation, was dissolved in water and titrated with 0.1 N HCl, using phenolphthalein as indicator. Calculating, from the total consumption of alkali, the quantity required for saponification of allyl methacrylate (the quantity of which had been calculated from the analysis mentioned above) we should obtain the consumption of alkali in the saponification of methyl methacrylate and consequently the quantity of this material. The divergences obtained in this way are quite large, as can be seen from Table 2.

SUMMARY

It has been shown that it is impossible to analyse copolymers of methyl and allyl methacrylates by determining the unreacted allyl methacrylate as allyl alcohol.

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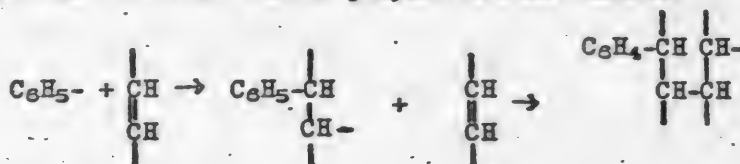
CONDITIONS OF CROSS-LINKING OF POLYMERS ¹

A. Ya. Drinberg, Sh. N. Golant and L. I. Goldfarb

Leningrad Lensoviet Technological Institute

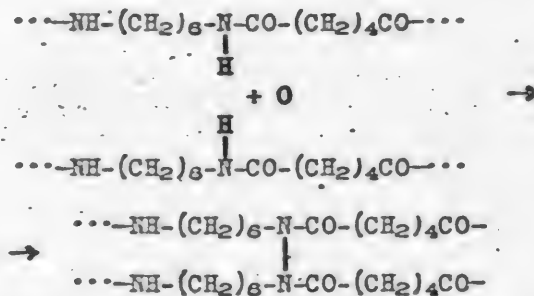
Published papers, in the main, have dealt with the question of the cross-linking of unsaturated monomeric compounds [1] and also of unsaturated linear polymers of the rubber type [2]. A detailed review of this work has been given by Rutovsky and Shur [3].

It is usually taken that the cross-linking of macromolecules is possible for those substances which have double bonds in their chains. Thus, for example, Tugov and Zaionchikovskiy [4] established that, in the presence of benzoyl peroxide, sodium butadiene rubber polymerizes as follows:



Dogadkin [5] showed that rubber, when oxidized by atmospheric oxygen, forms a spatial structure with oxygen bridges linking separate chains, in the course of which it loses its elasticity and ages.

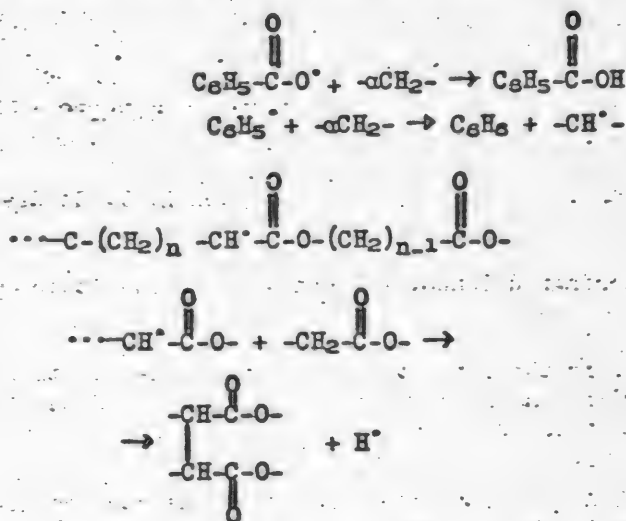
Another type of cross-linking was observed by Korshak and Rafikov [6] when investigating the transformation of polyamides on heating in the presence of atmospheric oxygen.



The reaction between saturated linear polymers has not been much studied. Becker [7] and Biggs [8] cross-linked linear polymers of condensation resins in the presence of benzoyl peroxide at 150-200°. The authors suggested that the benzoyl peroxide decomposes at temperatures above 105°, forming free radicals which activate the saturated ester chains. The combination of two ester macromolecules occurs through the α -carbon atoms.

¹) Communication I dealing with the spatial transformation of saturated linear polymers.

Becker deduced the following cross-linking scheme:



This paper deals with a study of the possibility of cross-linking films of saturated linear polymers: polybutylmethacrylate, polyvinylchloride, pervinylchloride and polythene.

EXPERIMENTAL

The polybutylmethacrylate had a specific viscosity in 1% solution of toluene, in an Ostwald viscosimeter, of 0.320-0.350. The tetramethacrylic ester of pentaerythrite, denoted PM, melted at 63-64° and had an ester number of 545.

The transformation of the linear to trimeric polymers was followed by the gradual diminution of the quantity of soluble fraction, by the rise of the softening temperature, of the hardness and other indexes of mechanical and electrical properties and, for films on glass and metal, by the increase in adhesion. Other indexes may also be selected. The solubility of the polymers was determined in a Soxhlet apparatus, for which the most active solvents were selected beforehand. We will come back to the study of other properties later.

The previously prepared solutions of polymer were: a 3% solution of polyvinylchloride in dichlorethane, a 10% solution of pervinylchloride in xylene, a 3% solution of polythene in benzene, a 30% solution of polybutylmethacrylate in xylene. Thus the polymer content was adjusted in accordance with its molecular weight.

As cross-linking agents, the following compounds were investigated: 1) the complete pentaerythrite ester of methacrylic acid; 2) the pentaerythrite ester of the fatty acids of flax oil; 3) diazoaminobenzene; and 4) benzoyl peroxide.

The choice of these compounds will be discussed in a later paper.

Transformation of the complete pentaerythrite ester of methacrylic acid to the trimeric polymer has already been described [9]. In air, at lower temperatures, this transformation goes through the stage of a peroxide as in the transformation of drying oils. On introduction of PM into a solution of linear saturated polymers it was observed that, on drying, part of the saturated polymer was also converted to the trimeric polymer.

It is known that the transformation of the pentaerythrite ester of the fatty

acids of flax oil on drying passes, as does that of drying oils, through a peroxide stage [10]; it was thought that in the presence of cobalt soaps these compounds would also have drying properties. However, investigation did not confirm this supposition. In this case, apparently, a specific behavior of the acid radicals was involved. It must be remembered that the average specific content of reactive groups in the fatty acids of flax oil is three times smaller than in methacrylic acid.

Diazoaminobenzene was used for cross-linking rubber. It was shown that even additions of 0.25 parts by weight changed the properties of the film. Investigation established that this cross-linking capacity was not effective for saturated linear polymers at temperatures of 100-150°. The films remained soluble. It is known that benzoyl peroxide has a cross-linking capacity at high temperatures [4, 5]. Preliminary experiments showed that in the presence of benzoyl peroxide considerable part of the linear polymer was converted to an insoluble condition.

The effect of the following factors on the process of cross-linking was investigated: temperature, duration of reaction, concentration of benzoyl peroxide and plasticizer.

1. The cross-linking of polybutylmethacrylate was carried on at 100-2000°, in the presence of 3% benzoyl peroxide on the weight of polymer. The quantity of insoluble polymer was determined by extraction with benzene. The cross-linking data are set out in Table 1 and Fig. 1.

TABLE 1

Effect of Temperature on the Process of Cross-linking with Benzoyl Peroxide

Temperature (in ° C)	100	120	150	160-170	170-180	180-190	190-200
Quantity of insoluble polymer	0	0	0	63-70	70-80	92	100

As can be seen from Table 1, the quantity of insoluble polymer increases with increase in temperature. This may be explained by an increase of the mobile activated macromolecules with increase of temperature, which increases the probability of their collision in a favorable attitude.

2. Investigations of the effect of the quantity of benzoyl peroxide showed that the optimum is at about 5% of benzoyl peroxide on the weight of linear polymer. Data are set forth in Table 2.

TABLE 2

Effect of the Quantity of Benzoyl Peroxide on the Cross-linking of Polybutylmethacrylate at 160-165°

Quantity of benzoyl peroxide (in %)	0	1	3	5	10
Quantity of insoluble polymer (in %)	27-28	32-40	66-77	75-78	75-80

The transformation of 27-28% of the polybutylmethacrylate, in the absence of any benzoyl peroxide, can be explained by the presence in the polymer residues of benzoyl peroxide added for polymerization of the monomer (0.3% introduced).

3. In order to study the effect of the duration of the process on the transformation of the linear polymer, a polybutylmethacrylate film with 3% benzoyl peroxide was exposed to temperatures of 170-180° for about six hours. The samples

were extracted with benzene and the quantity of insoluble polymer determined. The data are set forth in Table 3 and Fig. 2.

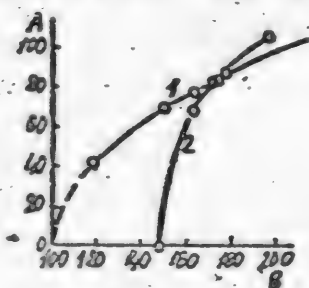


Fig. 1. Effect of temperature on the process of cross-linking of saturated polymers with benzoyl peroxide (3%).

A - % Transformation of linear polymer; B - temperature (in °C). 1 - Polythene; 2 - polybutylmethacrylate.

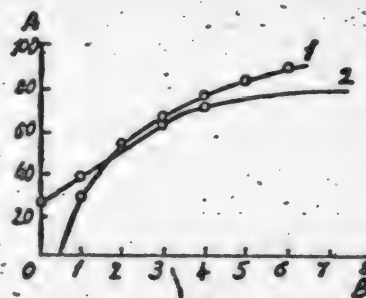


Fig. 2. Dependence of the quantity of polybutylmethacrylate converted on the duration of cross-linking and the quantity of benzoyl peroxide.

A - % Conversion of the linear polymer; B - time (in hours) and % benzoyl peroxide. 1 - Dependence on time; 2 - dependence on % of benzoyl peroxide.

With increase in the duration of the process the quantity of linear polymer converted increases.

TABLE 3

Dependence of the Quantity of Polybutylmethacrylate Converted on the Duration of the Process

Duration of the process (in hours)	0.5	1	2	3	4	5	6
Quantity of unconverted polymer (in %)	0	29	55-56	66	75-83	87-90	90

4. Films obtained by conversion of polybutylmethacrylate had a low elasticity. In order to raise this elasticity the effect of plasticizers was studied. At the same time the effect of plasticizers on the conversion of the polymer was studied, using castor oil, dibutylphthalate, tricresylphosphate. The transformation was effected at 170-180° and the data are shown in Table 4. It can be seen from this table that, as the quantity of the plasticizer increases, the quantity of trimer sharply decreases and the plasticity of the films increases. In polymers with 10% tricresylphosphate, but with no benzoyl peroxide, there was practically no cross-linking. However, such films are brittle, apparently as a result of depolymerization, (degradation of the polymer).

TABLE 4

Effect of Plasticizer (Tricresylphosphate) on the Cross-linking of Polybutylmethacrylate with Benzoyl Peroxide at 170-180° for 6 hours

Quantity of plasticizer (in %)	10	15	20	10	10	10
Quantity of benzoyl peroxide (in %)	5	5	5	0	3	10
Quantity of trimer (in %)	10	2.1	1.0	1.0	16	62

5. The effect of degree of polymerization of the linear polymer was studied on polybutylmethacrylate of different degrees of polymerization. The conditions of synthesis of these polymers are set out in Table 5.

TABLE 5
Conditions of Synthesis of Polybutylmethacrylate

No. of polymer	Quantity of butyl methacrylate monomer (in %)	Quantity of solvent (in %)	Quantity of benzoyl peroxide (in % on weight of monomer)	Conditions of polymerization		Specific viscosity of polymer
				Temp. in °	duration (in hrs)	
1	80	20	3	100-110	6	0.12
2	70	30	0.3	90-95	6	0.32
3	90	10	0.3	90-95	6	0.44

The effect of degree of polymerization on the conversion of the linear polymers is shown in Table 6.

TABLE 6
Effect of Specific Viscosity of Polybutylmethacrylate on its Transformation

No. of polymers	Specific viscosity	Total quantity of trimer formed at the expense of the linear polymer (in %) (cross-linking with benzoyl peroxide at 170-180°)	Quantity of trimer (in %) (cross-linking of PM at 100°)		
			total quantity	same quantity expressed on the linear polymer	in % of the linear polymer content in the film
1	0.12	39-44	39.0	18.0	23.3
2	0.32	50-56	61.5	38.5	50.0
3	0.44	75-84	85.0	52.0	67.5

From Table 6 it is evident that, as the degree of polymerization of the polybutylmethacrylate increases, the quantity of linear polymer converted increases. This phenomenon, apparently, is explained by the great probability of collisions of separate units of the longer macromolecular chains, and consequently by the greater probability of cross-linking with the formation of a trimeric structure.

SUMMARY

1. The possibility of converting soluble linear polybutylmethacrylate polymers to the insoluble state has been shown.
2. As the concentration of benzoyl peroxide, time of reaction and the temperature increase, the rate of conversion of the linear polymer to the insoluble state increases.
3. With increase in the concentration of plasticizer, the degree of conversion to the insoluble polymer sharply decreases.
4. The molecular weight of the original linear polymer has a large effect on the conversion. It can be supposed that, with increase of the molecular weight, the percentage converted to the trimeric polymer increases.

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CONDITIONS STIMULATING THE FORMATION OF CARBOXYLIC ACIDS IN THE OXIDATION OF KEROSENE FRACTIONS

V. K. Tsyskovsky and T. N. Shcheglova

Published work on the oxidation of liquid petroleum hydrocarbons [1] indicates that oxidation, in the great majority of cases, follows several different paths. If from these the main ones are separated out, they can be divided into two types:

1) those tending towards the formation of aldehydes, normal carboxylic acids and ester acids (soluble in petrol).

2) those in which there is a transition of the normal carboxylic acids to hydroxy compounds of different types and into internal esters.

Up to the present it has been impossible to avoid obtaining, in the oxidation of petroleum hydrocarbons, oxidation products resulting from both types of reaction, in which the second type appears to predominate over the first.

The formation of different oxygenated compounds can be explained above all by the complex chemical composition of the oxidizing hydrocarbons and by differences in their chemical and physical properties. Apart from this, since oxidation occurs mostly in the liquid phase, the substances formed do not leave the sphere of reaction and it is impossible to avoid subjecting them to further action by atmospheric oxygen.

The result of this is that the oxidation product obtained, as a rule, is a mixture of different compounds, mainly carboxylic acids and their derivatives, hydroxy and ester acids.

In the oxidation of liquid hydrocarbon mixtures (of the type of kerosene or vaseline) the relation between the first and second types of acid varies between 1.4:1 and 3.6:1 [1,2]. Thus, in the mixture of acids obtained in the oxidation experiments by different investigators, the content of the first type of oxidation product does not exceed 77% in particularly successful, but unreproducible, cases.

As hydroxy acids seem to be unavoidably formed in the oxidation of carboxylic acids and since, on account of the relatively small knowledge about this process, their separation is complicated, the mechanism of oxidation has for a long time remained unexplored.

By close study of the material, accumulated over many years, relative to the oxidation of liquid petroleum hydrocarbons, we came to the conclusion that the correspondence between carboxylic acids and their hydroxy derivatives is variable and can be changed by changing the conditions of the process. Petrov [2] also foresaw that the conditions of the process are of primary importance, saying: ".....It is self-evident how important all the improvements and achievements made in the first stage of production will be, i.e. the elucidation of the conditions of oxidation with corresponding starting materials."

Much later [3], in the study of separate factors which affect the oxidation of liquid petroleum hydrocarbon mixtures, one of us succeeded in finding condi-

ions under which the reaction is directed mainly along one path, with the formation of a predominant quantity of a single type of oxidation product (ester acids). This allowed us to draw the conclusion that, since conditions stimulating the formation of secondary products of oxidation can be created, then it should be possible also to find those which would stimulate primary reactions, resulting in the preparation of a mixture of acids containing 90% and more of carboxylic acids. (We shall maintain this provisional term 'carboxylic' acids in the rest of this paper).

By systematic work in this direction, the conditions were determined in which it was possible to obtain primary products with a high carboxylic acid content.

In the present work, we aim to show, by the example of the oxidation of kerosene fractions, how the factors affect the direction of the process along the desired path.

It is not desirable to repeat and describe the elements of the process, established earlier, which ensure the highest yield of carboxylic acid, such as the degree of purification of the petroleum hydrocarbon mixture from the aromatic hydrocarbons contained in it, lowering the temperature of the process; we shall examine here in succession the following: 1) the group composition; 2) molecular weight of the substrate; 3) concentration of catalyst; 4) air rate through the reactor; and 5) the extent of the oxidation and the effect of withdrawing carboxylic acids formed from the sphere of reaction.

EXPERIMENTAL

The oxidation of the substrate under examination was carried out in the liquid phase in the glass laboratory columns already described [4].

The experiments were carried out by changing one of the variables at a time, keeping all the others constant. The oxidation of any raw material (close or wide kerosene cuts freed from the main quantity of aromatic hydrocarbons) was carried out at 120° for 8 hours. Such conditions of experiment were selected because they do not promote secondary reactions on a large scale, and thus ensure the formation of carboxylic acids at a sufficiently high rate. At the given temperature and duration of the process it was easier to intensify the effect on the course of oxidation, of one or other of the conditions.

Group composition of the substrate. For studying the effects of the group composition of the starting materials, we oxidized various separate kerosene fractions which were nearly identical in physical properties (density, molecular weight, boiling range, etc.,) and which did not differ from one another in their group composition (Table 1).

TABLE 1

Effect of Group Composition of the Raw Material

Group composition of the fraction (in wt. %)			Yield (in wt. %)		Carboxylic acids content in the acid mixture (in wt. %)
alkanes	cyclanes	aromatic hydrocarbons	carboxylic acids	ester acids	
64.5	35.15	0.35	28.1	16.7	60.8
49.4	50.13	0.47	24.5	18.9	56.5
36.3	63.19	0.51	24.1	19.1	56.0
31.37	68.10	0.53	17.3	21.5	44.6

Note: The data were obtained with an air rate of $V = 5$ cm/sec., and at an active catalyst concentration $K = 0.05\%$ (on metal).

With increase in the cyclanes content in the fraction from which aromatics had been eliminated (though not completely), the quantity of carboxylic acids obtained on oxidation tended in general to decrease. This can easily be explained by the fact that cyclic hydrocarbons oxidize at a higher rate.

There is no doubt, however, that this correlation does not always apply, (as is evident from the table), on account of the differences in chemical structure of the cyclanes present in the mixture being oxidized, and particularly in those cases, where the cyclic compounds have one or several long aliphatic side chains; such an effect shows the presence of a known amount of aromatic hydrocarbon, which for several reasons cannot be withdrawn from the fraction being oxidized.

None the less it can be taken that the quantity of carboxylic acids decreases as the cyclanes content in the substrate increases.

Molecular weight of the initial raw materials. The size of the molecule of substrate determines, in the first place, its physical state during oxidation.

Lighter molecules, which are extracted from the substrate by a stream of air, are in essence not oxidized in the liquid but in the vapor phase [4]. Hence the time of contact of such molecules with atmospheric oxygen is very much shorter than is that of molecules which remain in the liquid phase. Decrease in the time of contact in turn induces a higher rate of reaction.

TABLE 2

Effect of Molecular Weight of the Fraction.

Mol.wt. of fraction	Group composition (in wt. %)			Yield (in wt.%) on the weight of substrate		Carboxylic acids content in the mixed acids (in wt. %)
	alkanes	cyclanes	aromatic hydrocarbons	carboxylic acids	hydroxy acids	
145	61.5	36.0	2.5	2.3	86.3	2.6
157	65.7	32.15	2.15	4.6	75.7	5.73
163	68.3	29.8	1.9	10.8	53.4	16.8
179	60.9	36.9	2.2	18.7	28.9	49.8
186	69.4	28.0	2.6	23.5	16.3	59.5
195	66.1	31.85	2.05	31.3	10.7	74.6
215	68.7	28.86	2.44	38	4.5	89.4

For this reason the lighter molecules rapidly oxidize, converting to secondary reaction products, mainly ester acids

Consequently, the more homogeneous the composition of the substrate, i.e. the more it is composed of physically similar molecules, the more homogeneous in type will be the oxidation products.

In fact, if a number of fractions, containing approximately equal quantities of hydrocarbons of one or another type, but differing in their average molecular weight, are oxidized (in Table 2), then it will be found that the correlation indicated is fully substantiated.

If the fractions are oxidized under conditions in which the possibility of vapor phase reaction is excluded, then a different state of affairs is found, i.e., the quantitative relationship between the acids formed remains constant and does not depend on the average mol. wt.

Since it is, in practice, extremely difficult to eliminate the possibility of forming a vapor phase during the oxidation of such hydrocarbon mixtures as

kerosene fractions, the mol. wt. of the latter will always determine the quantitative aspects of oxidation, not to mention, of course, its qualitative aspects.

Thus, in order to oxidize wide-cut kerosene fractions to produce carboxylic acids, their molecular weight must be increased and their boiling range reduced.

Concentration of catalyst. It has been established that, to increase the rate of the reaction and to shorten the time of the process, it is expedient to use an active catalyst. The introduction of such a catalyst into the substrate in turn hinders the transformation of the primary products into secondary ones.

If any high molecular weight, wide-cut kerosene fraction is oxidized under the optimum conditions, changing only the catalyst concentration, it is observed that the carboxylic acids formed and their qualitative indexes vary continuously (Table 3).

This indicates that, with variation in the concentration of the active catalyst, the direction of the oxidation itself varies continuously.

At the optimum conditions for a given temperature, the process goes in the direction of producing simpler compounds. In extreme cases, catalyst concentrations are found at which the production of hydroxy acids and their esters is most favored.

TABLE 3

Effect of Catalyst Concentration

Concentration of active catalyst (on metal, in wt. %)	Yield (in wt.%)		Total quantity of carboxylic acids in the mixture	Molecular wt. of the carboxylic acids
	ether acids	carboxylic acids		
0.003	2.8	15.0	84.2	333
0.005	3.0	16.4	84.6	309
0.007	3.0	18.8	86.2	311
0.02	3.0	22.4	88.2	300
0.03	3.6	24.8	87.4	275
0.05	5.4	23.0	81.0	272
0.09	11.2	18.2	62.0	261
0.11	15.2	1.3	51.8	—

The formation of mixtures of acids with the maximum carboxylic acids content is thus determined by the optimum catalyst concentration, which in its turn depends on the temperature. The largest carboxylic acids content in the mixture is observed only when small catalyst concentrations are used, and when its concentration increases the carboxylic acids concentration falls sharply.

In this particular case we come up against a typical example of the transformation of carboxylic acids to hydroxy compounds

Air rate through the reaction. This factor is directly related to the molecular weight of the substrate and, in addition, determines the active oxygen concentration.

As the air rate increases not only is the reaction rate observed to increase, but the carboxylic acids content increases, when a kerosene fraction of any composition is oxidized (with a minimum content of those molecules tending to vapor phase reaction) (Table 4).

The carboxylic acid contents shown in Table 4 can only be realized at such

high air rates with some changes in the oxidation technology, by which the quantity of oxidizing hydrocarbons going into the vapor phase is artificially lowered. It should be noted that the air rate at which such a result is obtained (91%) is far from the optimum one, however at present a number of technical difficulties prevent us from basing the process of oxidation of hydrocarbons on the optimum air rates.

TABLE 4

Yield of Carboxylic Acids as a Function of the Air Rate

Air rate through the reactor (cm/sec)	Yield of carboxylic acids (in wt. % of the total acid)
5.5	75.0
6.5	78.5
7.0	80.0
8.2	82.2
9.6	84.7
10.5	86.8
11.7	88.0
12.6	91.0

by alkalification) and the unoxidized residual hydrocarbons are again allowed to oxidize, then we do obtain a sharp increase in the absolute yield of the carboxylic acids and in their proportion in the mixture of acids (Table 6).

TABLE 5

Effect of the Duration of the Oxidation Process

Duration of the oxidation process (in hrs)	Yield (in wt.%)		Yield of carboxylic acids (in wt.% of the total saponified acids)
	carboxylic acids	ester acids	
3	11.7	0.8	93.5
5	14.4	1.3	91.8
6	15.0	1.8	89.3
8	15.8	2.0	84.3
12	21.6	19.6	52.5
14	21.0	20.0	52.5

All this shows that by suitable choice of the oxidation conditions extremely high yields of 92% (and higher) purity carboxylic acids can be obtained in the oxidation of kerosene fractions.

In conclusion we should like to convey our thanks to M. A. Sazanova and N. P. Zabelina, for executing the practical work.

Duration of reaction and effect of withdrawing the carboxylic acids formed from the sphere of reaction.

If the variation of the process with time is followed, then it is easily seen that, after a time, the quantity of carboxylic acids formed in the mixture gradually falls (Table 5); the highest content of carboxylic acids in the mixture of acids is found only in the first hour of oxidation. Consequently, even at the optimum conditions it is difficult to protect the acids formed against subsequent change. If the carboxylic acids are withdrawn from the sphere of reaction after a known interval of time, (for example

TABLE 6

Effect of Withdrawing Carboxylic Acids from the Sphere of Reaction

Description of process	Total time of process (in hrs)	Yield (in wt.%)		Carboxylic acids content in the mixture (in wt.%)
		carboxylic acids	hydroxy acids	
Extension of oxidation in the liquid phase	12.0	20.6	4.8	81.2
Stepwise extraction of acids from zone of reaction every 3 hours..	12.0	46.1	3.78	92.6

SUMMARY

It has been established that, by creating optimum conditions for the oxidation of kerosene fractions of definite group composition, a mixture of acids can be obtained in which there is 92 wt. % and more of carboxylic acids.

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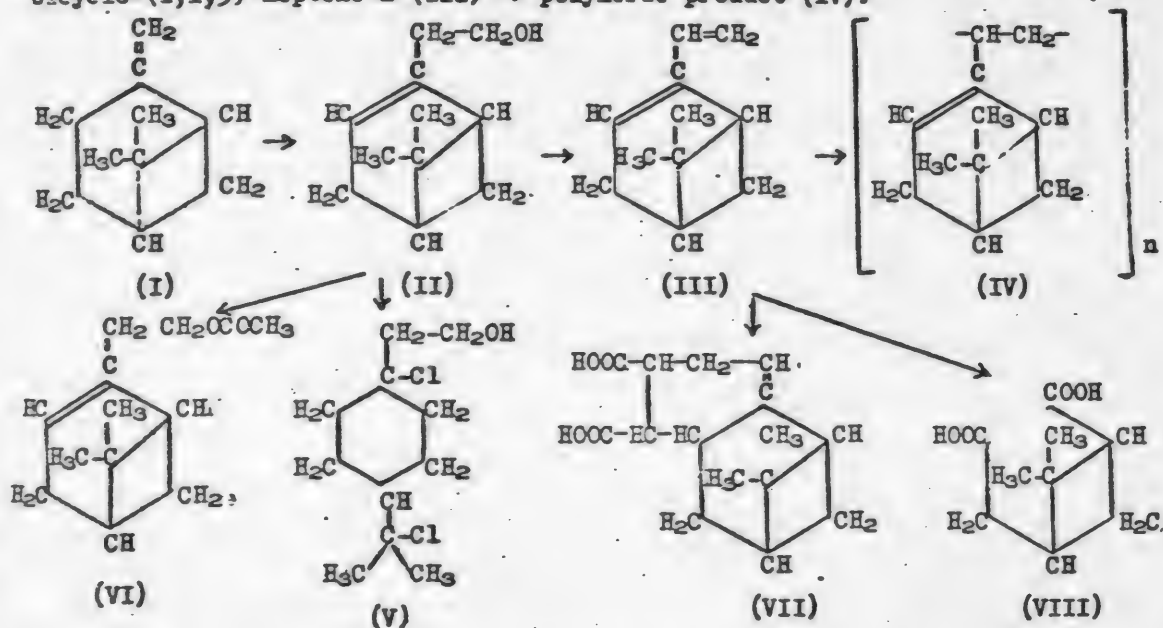
PREPARATION OF NOL AND ITS DERIVATIVES

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The object of this work has been to prepare compounds of the vinyl type $\text{CH}_2=\text{CHX}$ in the terpene series and to polymerize them subsequently to form high molecular products.

To carry out this investigation we proceeded as follows: β -pinene (I) \rightarrow 6,6-dimethyl-2-ethylol-bicyclo-(1,1,3)-heptene-2 (II) \rightarrow 6,6-dimethyl-2-vinyl-bicyclo-(1,1,3)-heptene-2 (III) \rightarrow polymeric product (IV).



There is 6-9% β -pinene in turpentine derived from fir, as obtained in the USSR, and up to 42% in turpentine from spruce.

EXPERIMENTAL

Preparation of β -pinene [1]

In our work β -pinene was separated from natural turpentine, obtained from the common fir, and having the following characteristics:

d_4^{20} 0.8611; n_D^{20} 1.4700; $[\alpha]_D^{20}$ 17.31°; boiling range 158-176°.

The turpentine was distilled through a column, 100 mm diameter and height 5.5 m, filled with Raschig rings, diameter 6 mm and height 10 mm with reflux number 6-8. The characteristics of the fractions obtained are set forth in Table 1.

These fractions were redistilled at 20 mm Hg through a column of diameter 50 mm, height 2 m, filled with 5 mm diameter turns of 1.0 mm thick aluminium wire, with reflux number 12-15. For further work the fractions whose constants are given in Table 2 were taken.

TABLE 1

Characteristics of Fractions Obtained by Distillation of Natural Turpentine.

Fraction No.	d_4^{20}	n_D^{20}	$[\alpha]_D^{20}$	$\frac{a_v}{a_j}$	$\frac{a_f}{a_c}$
19	0.8634	1.4673	+6.28°	1.018	2.661
20	0.8653	1.4678	-4.59	0.965	0.676
21	0.8653	1.4683	-6.36	1.009	0.969
22	0.8646	1.4675	-2.90	0.915	0.237
23	0.8639	1.4670	+1.78	1.420	8.602
24	0.8632	1.4665	+4.13	1.254	3.470

Thus a fraction with the constants:

$$d_4^{20} = 0.8681; n_D^{20} 1.4806; [\alpha]_D^{20} 15.45^\circ,$$

was obtained, containing 90.2% β -pinene, by the oxidation of which nopinic acid (b.p. 125-126°) and nopinone (b.p. 207.2°) were obtained.

Preparation of Nopol [II]

By condensing β -pinene with paraformaldehyde [1] the alcohol $C_{11}H_{17}OH$, 6,6-dimethyl-2-ethylol-bicyclo-(1,1,3)-heptene-(2),

provisionally called 'nopol' was obtained. The paraformaldehyde contained 93.75% formaldehyde (determined by the iodine method), hence the calculations were made corresponding to an enhanced molecular weight of 32.02. In all experiments, after the end of the reaction and cooling down the autoclave, a small quantity of gas was released and a black sticky deposit remained on the surface of the autoclave in extremely small quantity, mostly in Experiment No.1 (Table 3), i.e., when the starting material was poorer in β -pinene. The reaction product was transparent, slightly yellow and had a strong smell of formaldehyde. It was washed with water and fractionated in vacuum.

TABLE 2

Characteristics of Fractions Obtained by Redistillation of Turpentine

Expt. No.	d_4^{20}	n_D^{20}	$[\alpha]_c^{20}$	$[\alpha]_D^{20}$	$[\alpha]_j^{20}$	$[\alpha]_v^{20}$	$[\alpha]_f^{20}$	$\frac{a_v}{a_j}$	$\frac{a_f}{a_c}$
1	0.8632	1.4745	+ 4.55	+ 6.36	+ 6.66	+ 8.25	+ 11.73	1.238	2.577
2	0.8655	1.4773	- 2.83	- 2.93	- 3.18	- 2.57	- 1.05	0.808	0.371
3	0.8681	1.4806	-13.09	-15.45	-15.85	-16.67	-18.04	1.052	1.370

The optimum conditions of condensation, as can be seen from Table 3, are: a) temperature 180-200°; b) 3-fold molecular excess of paraformaldehyde relative to β -pinene; and c) duration of operation six hours.

TABLE 3

Data on Condensation of β -Pinene with Paraform

Expt. No.	Quantity of fraction, (g.)	Fraction No.	β-Pinene content			Charge			Molar ratio β-Pinene: Paraform	Conditions of condensation			Nopol obtained (fraction boiling at 104-108°)	
			(g.)	(g.)	(Mole %)	Paraform		Molar ratio (g.)		Temperature (°C)	Pressure (mm.)	Duration (hr.)	(g.)	(Mole %)
						(g.)	(Mole %)							
1	191.0	1	59.8	114.2	0.839	42.2	1.318	95.5	0.636	176-185	20-25	6	50.9	44.6
2	129.8	2	72.6	94.2	0.692	67.2	2.198	147.3	0.315	198-200	83-100	6	54.5	47.4
3	250.0	3	90.2	225.5	1.658	168.8	5.209	212.5	0.318	196-200	20-32	6	281.0	51.07
4	250.0	3	90.2	225.5	1.658	168.8	5.209	225.5	0.318	195-200	20-36	6		
5	250.0	3	90.2	225.5	1.658	168.8	5.209	225.5	0.318	185-195	20-34	6		
6	250.0	3	90.2	225.5	1.658	168.8	5.209	225.5	0.318	185-190	20-32	6	361.1	57.8

Under these conditions α -pinene, camphene and dipentene scarcely react with formaldehyde.

The product of Operations 1 - 4 (Table 3) was fractionated through a column, diameter 20 mm and height 60 cm filled with 4 mm diameter turns of aluminum wire 1 mm thick, and provided with an electrical heater, with reflux number 12-15 and at a pressure of 10 mm Hg. The results of the distillation are given in Tables 4 and 5.

TABLE 4

Results of Distillation of Products from Operations 1 and 2

Fraction No.	Quantity (in g)	Temperature (in °)	Pressure (in mm Hg)	n_D^{25}	α_D^{14}	d_4^{25}
Product of 1st operation						
1	44.9	to 45	10	1.4677	20 + 16.24	-
2	21.4	to 61	10	1.4790	20 + 2.82	-
3	4.3	to 108	10	1.4869	-	0.9017
4	9.6	108.0-110.5	10	1.4879	-19.60	0.9632
5	28.9	110.5-112.0	10	1.4983	-22.84	0.9649
6	12.4	112.0-114.0	10	1.4989	-29.10	0.9662
Product of 2nd operation						
1	14.4	to 80	10	1.4725	+ 3.30	-
2	6.3	80-108	10	1.4820	- 12.82	0.9304
3	24.4	108-110.5	10	1.4873	- 20.46	0.9646
4	15.1	110.5-112.0	10	1.4885	- 22.28	0.9654
5	15.0	112.0-114	10	1.4890	- 22.05	0.9673

To get a purer fraction of the alcohol a special column was set up, having a diameter of 20 mm and a height of 1 m, filled with 3-5 mm diameter rings of 0.75 mm thick aluminum wire, and with an electric heater. The reaction mixtures from Operations 5 and 6 were fractionated through this column (Table 6), with a reflux number of 12-15 and at a pressure of 10 mm Hg.

TABLE 5

Results of Distillation of Products from 3rd and 4th Operations

Fraction No.	Quantity (in g)	Temperature (in °)	Pressure (in mm Hg)	n_D^{25}	α_D^{25}	d_4^{25}
1	-	100-108	10	1.4817	-16.62	-
2	25.4	108-109.0	10	1.4862	-21.76	0.9614
3	74.5	109-110.2	10	1.4869	-22.48	0.9649
4	112.2	110.2-111.5	10	1.4882	-23.40	0.9667
5	68.9	111.5-114.0	10	1.4893	-23.32	0.9670

130 - 150 g of product boiling above 114° at 10 mm Hg, a dark viscous liquid, was obtained from two experiments; it was not investigated further.

Repeated distillations of the fraction boiling at 110-111° at 10 mm Hg, through a column set up for the distillation of nopyl acetate, with a reflux number of 12-15 and at 10 mm Hg, gave pure 6,6-dimethyl-2-ethylolbicyclo-(1,1,3)-heptene-(2). Its constants were:

b.p. 110.5° at 10 mm; d_4^{20} 0.9681; n_D^{20} 1.4935; $[\alpha]_D^{20}$ 27.89; Found MR_D 49.91.
 $C_{11}H_{17}OH$. Calculated: MR_D 49.66.

4.205 mg substance: 12.267 mg CO_2 ; 4.098 mg H_2O .

4.558 mg substance: 13.306 mg CO_2 ; 4.462 mg H_2O .

Found % : C 79.42, 79.55, H 10.83, 10.86

$C_{11}H_{17}OH$. Calculated % : C 79.52; H 10.84.

The molecular weight was determined by the depression of the freezing point of benzene: 163.2, 165.4; calc. for $C_{11}H_{17}OH$ = 166.15.

The alcohol was a thick liquid, colorless and odorless, reminiscent of glycerine in external appearance, insoluble in water and dissolving well in ether, acetone and ethanol.

TABLE 6

Results of Distillation of Products from Operations 5 and 6

Fraction No.	Quantity (in g)	Temperature (in °)	Pressure (in mm Hg)	n_D^{20}	α_D^{20}	d_4^{20}
1	28.0	108-109.0	10	1.4878	-22.20	0.9647
2	29.2	109-109.5	10	1.4880	-23.58	0.9658
3	31.3	109.5-110.0	10	1.4885	-23.99	0.9664
4	29.5	110 -110.2	10	1.4894	-24.10	0.9669
5	23.1	110.2-110.5	10	1.4898	-24.12	0.9670
6	30.5	110.5-111.0	10	1.4905	-24.20	0.9673
7	31.5	110.0-111.5	10	1.4903	-24.20	0.9673
8	32.2	111.5-112	10	1.4904	-24.20	0.9674
9	33.5	112 -112.5	10	1.4901	-23.70	0.9683
10	21.2	112.5-113.0	10	1.4895	-23.38	0.9687
11	26.1	113.0-114.0	10	1.4890	-22.94	0.9695

Preparation of 1,8-dichloro-7-p-menthanecarbinol

33.3 g of Fraction No.5 (Table 5) was treated with 99.5 g of concentrated HCl. The mixture was shaken for 15 minutes while being cooled. The upper oily layer was separated, and after 5 days standing crystals began to precipitate from it. When the mass was cooled with ice the oily layer was converted to a paste. It was sucked out three times and recrystallized from petroleum ether. Acicular white crystals of 1,8-dichloro-7-p-menthanecarbinol were obtained:

M.p. 74-75°. Chlorine content: Found 29.16%, calculated for $C_{11}H_{20}OCl_2$ 29.65%.

Preparation of nopyl acetate (VI)

50 g of Fraction No.4 (Table 5), 150 g of acetic anhydride, and 10 g of molten sodium acetate were boiled for an hour. The reaction mixture was diluted with water, the ether separated, dried and fractionated in a column having a diameter of 10 mm and height 1.3 mm filled with glass rings, diameter 3.5 mm, thickness of glass fiber 0.8 mm, reflux number 12-15 and at 10 mm Hg. The results of the distillation are set forth in Table 7.

TABLE 7

Results of Distillation of Ether

Fraction No.	Quantity (in g)	Temperature (in °)	Pressure (in mm Hg)	n_D^{25}	α_D^{23}	d_4^{25}
1	7.7	to 114	10	1.4860	-21.58	0.9621
2	17.3	114-118	10	1.4793	-19.62	0.9709
3	11.7	118-118.2	10	1.4703	-20.85	0.9772
4	8.5	118.2-119	10	1.4713	-20.69	0.9768

The product boiling above 119° at 10 mm Hg was a dark and very viscous liquid. weighing 12 g; it was not further investigated.

Nopol acetate boiled at 118° at 10 mm Hg and had the following constants:

$$d_4^{25} 0.9772; n_D^{25} 1.4708; [\alpha]_D^{23} - 21.33^\circ.$$

Molar refraction MR_D : found 59.39; calculated for $C_{11}H_{17}OCOCH_3$ 59.02. Sapon. number: Found 268 and 265; calculated for $C_{11}H_{17}OCOCH_3$ = 269.

Preparation of the Acid Phthalate of Nopol

10 g of Fraction No.5 (Table 6) whose OH group content by Tserevitinov's method was 8.25% (OH content for pure nopol 10.23%), 9.5 g of phthalic anhydride and 10 g of benzene were heated on a boiling water bath for 2 hours. The acid phthalate of the alcohol formed was a viscous, not very mobile, liquid which made its purification very difficult. The ether was saponified with alcoholic alkali, separated from the alcoholic solution with water, extracted with ether, steam distilled and fractionated in vacuum. 6 g of alcohol was obtained with the constants:

$$n_D^{25} 1.4919; [\alpha]_D^{25} - 26.74^\circ; d_4^{25} 0.9674; \text{OH group content (Tserevitinov) } 9.28\%.$$

SUMMARY

1. By condensation of β -pinene with formaldehyde an alcohol $C_{11}H_{17}OH$ was obtained in yield of 57.8% which, by quantitative calculations and by structural indications, appears to be a derivative of α -pinene. Its constants are density d_4^{20} 0.9681; refractive index n_D^{20} 1.4935; specific rotation $[\alpha]_D^{20}$ - 27.89°; and b.p. 110.5° (at 10 mm).

The acetate of the alcohol was obtained with acetic anhydride and its constants are b.p. 118° (at 10 mm); density d_4^{25} 0.9772; refractive index n_D^{25} 1.4708 and specific rotation $[\alpha]_D^{23}$ - 21.33°. With concentrated HCl, white acicular crystals of 1,8-dichloro-7-p-menthane-carbinol, with an m.p. of 74-75° were obtained.

2. For the condensation of β -pinene with paraformaldehyde the optimum conditions are a) temperature 180-200°; b) 3-fold molar excess of paraformaldehyde on β -pinene; and c) presence of ethyl alcohol.

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BRIEF COMMUNICATIONS

PRODUCTION OF TABLE SALT FROM THE BRINES OF THE LARGE MANNICH (GUDILO)

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In the basin of the river Mannich there is a chain of salt lakes, which have served in the past, and still partly serve, as sources of table salt. The composition of the waters of these lakes, their hydrography, the conditions of feeding them from the reserves of salt in the soil, and their rational industrial exploitation have so far not been worked out in any detail.

The largest of these lakes is the Large Mannich, (estuary of the Gudilo) the area of which at high water, according to measurements by Kalesnik [1] is approximately 800 km²; according to other information it has a length of 125 km and a width of 1-10 km.

In dry years, with continuous strong winds, evaporation of a small quantity of water occurs from one end of the lake to the other, whereby, depending upon the strength and direction of the wind, and the rapidity with which it changes direction, the movement of the water in the lake can be very rapid. In the course of a few minutes a part of the lake area, previously dry, becomes covered with water to quite a considerable depth. In just the same way an expanse, previously occupied by water, dries up rapidly. The lake has no constant course and the movement of the water masses is solely due to the action of the winds.

The comparatively narrow ravine occupied by Lake Gudilo is the remainder of a sea channel which, in a previous geological epoch, served to unite the Pontiac sea, then occupying the site now occupied by the Black and Azov seas, with the Aral-Caspian sea.

The water of the Gudilo is so highly mineralized that its salt content exceeds that of the Pacific ocean. This becomes obvious in a dry period, when the water is converted to a saturated salt solution (brine).

During very dry periods parts of the lake floor become covered with a white skin of table salt. The floor of the lake is composed of dense salt-containing clays, and is covered with an upper layer (semi-liquid ooze).

EXPERIMENTAL

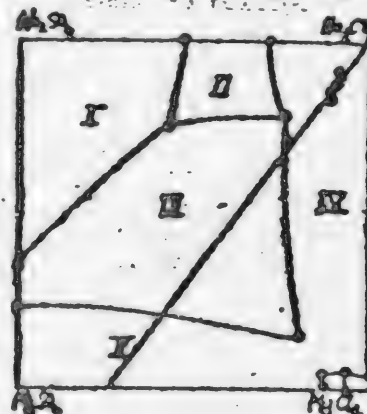
We have made an investigation of the brine of Lake Gudilo. The brine was collected by an old scientific collaborator of the Hydrochemical Institute of Veselovsky on September 15th, 1948. We set ourselves the aim of elucidating the process of concentration of the natural brine and the separation of the solid phase on evaporation. For this purpose quantities of 1 liter of the liquor were placed in a crystallizer and evaporated at 28-30°.

Chemical tests were made to follow the change in concentration of the liquor. Cl⁻, SO₄²⁻, Mg²⁺ were analyzed by the methods described by Kashinsky and Slavsky [3], and Na⁺ calculated by difference.

The solid phase separated was examined by crystallo-optical means and by subsequent chemical analysis. The experimental data are set forth in the Table.

Change in Composition of Brine on Evaporation

Expt. No.	Density	Concentration (in wt %)					Salt content (in wt %)			Salt (mol %)		
		Cl ⁻	SO ₄ ⁼	Mg ⁺⁺	Na ⁺	Cl ⁻	SO ₄ ⁼	Mg ⁺⁺	Na ⁺	NaCl	MgCl ₂	MgSO ₄
1	1.233	13.07	5.49	1.758	7.77	0.368	0.144	0.338	13.07	1.53	4.73	19.33
2	1.24574	12.81	5.78	1.76	7.72	0.360	0.144	0.336	14.23	1.02	5.09	20.34
3	1.2572	13.14	6.12	1.84	7.95	0.370	0.151	0.346	14.68	1.00	5.40	21.08
4	1.2634	13.14	6.43	2.10	7.61	0.370	0.172	0.331	14.24	1.66	5.75	21.65
5	1.2685	13.14	6.43	2.25	7.36	0.370	0.185	0.320	13.88	2.15	5.85	21.88
6	1.2788	13.06	6.07	2.38	7.33	0.367	0.195	0.319	13.95	2.11	6.43	22.49
7	1.2812	12.64	8.10	2.64	7.06	0.356	0.217	0.307	13.70	2.15	7.51	23.36
8	1.2827	12.89	8.07	3.11	6.34	0.363	0.255	0.276	12.99	4.13	7.93	25.05
9	1.2827	12.97	8.02	3.42	5.77	0.365	0.281	0.251	11.51	5.23	7.66	24.40
												89.2
												14.9
												5.8



Quaternary crystallization diagram of common salt from lake Gudilo brine.

- 1 - $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$;
- 2 - Na_2SO_4 ;
- 3 - $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$;
- 4 - NaCl ;
- 5 - $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

During evaporation the sodium chloride in the solution remained fairly constant in concentration; the quantity of MgCl_2 and MgSO_4 slightly increased. As the concentration proceeded the viscosity of the solution increased considerably, and at the end of the evaporation the brine had reached a syrupy consistency.

If the data obtained are plotted on a quaternary diagram, following Janecke, it is noted that variations in the composition of the Lake Gudilo brine correlates with the crystallization paths. The path followed by the solution in crystallization starts from the Na_2Cl_2 corner, and proceeds downwards towards the magnesium side of the diagram (Fig. 1.)

The points plotted on the Figure for the salt liquor during evaporation are clustered only in the NaCl field, showing how stable is the separation of

pure salt.

Pure NaCl crystallizes out from the liquor from the start of the concentration process, close to the line joining NaCl to astrakanite. The contamination of the table salt with sulfates occurs only when the points for the liquor approach the point uniting the crystallization of chloride with that of sulfates. With further evaporation the points are directed towards the line of the triple point of astrakanite, epsomite, and halite. The crystallization line most nearly approaches the $\text{Na}_2\text{Cl}_2\text{-MgCl}_2$ line, which corresponds to the process for obtaining the largest quantity of pure salt from the given liquor.

Such a method of crystallizing NaCl from the liquors of Lake Gudilo is very reminiscent of the process of crystallizing table salt from the liquors of lake Yarov (Kulundinskaya steppe) mentioned by Makarov [4]. An analogous method of crystallizing NaCl from the sulfateless brine of Lake Ebeit was mentioned by I. Druzhinin [5].

96 g of good quality table salt separated from 800 ml of the liquor of Lake Gudilo on evaporation. At the end of the evaporation the solid phase consisted of NaCl having 1/9th of the total volume taken, and the sulfate concentration was extremely small.

It must be concluded from our results that table salt of high quality can be obtained from Lake Gudilo not only by natural precipitation, as has been practiced right down to our own times, but also by simple evaporation of the solution.

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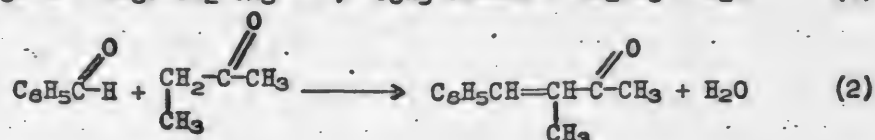
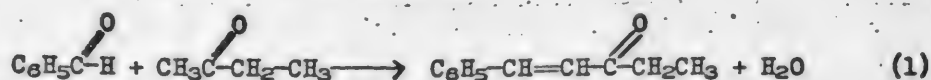
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EFFECT OF THE REACTION SOLVENT ON THE CONDENSATION OF METHYL ETHYL KETONE WITH BENZALDEHYDE

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The condensation of methyl ethyl ketone can follow two paths, depending on the solvent, through the methyl group or the methylene:



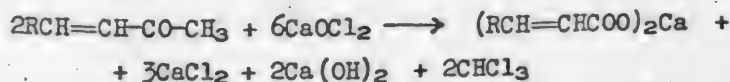
However, contradictory opinions are expressed in the literature about the effect of the solvent on the reaction. Thus, for example, Harries and Muller [1], noted that in acid methyl ethyl ketone reacts with benzaldehyde through the methylene group, but in alkaline solution through the methyl group. In their book "Organic Chemistry" Shlenk and Bergman [2] say the opposite, i.e. that in acid solution the reaction goes according to Scheme (1), and in alkali, according to Scheme (2).

By condensing benzaldehyde with methyl ethyl ketone we came upon a fact which contradicts the opinion expressed by Shlenk and Bergman.

In our investigation, the compound $\text{C}_6\text{H}_5\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CO}-\text{CH}_3$ was formed not in

alkaline but in acid solution. To demonstrate this we made use of the fact, reported by Staermer and Weln [3], that sodium hypochlorite is a sensitive means for detecting ketones of this type $\text{RCH}=\text{CH}-\text{CO}-\text{CH}_3$. This oxidant splits ketones in acid and chloroform according to the equation: $\text{RCH}=\text{CH}-\text{COCH}_3 + 3\text{NaOCl} \longrightarrow \text{RCH}=\text{CHCOONa} + \text{CHCl}_3 + 2\text{NaOH}$.

In our investigation we achieved the same result, replacing sodium hypochlorite with bleaching powder. In this case the oxidation follows the path:



Thus we established that, if the condensation of benzaldehyde with methyl ethyl ketone is conducted in an acid environment, compounds are formed which give, with bleaching powder, chloroform and α -methylcinnamic acid, which can only happen if the ketone is condensed with the formation of $\text{C}_6\text{H}_5\text{CH}=\underset{\text{CH}_3}{\text{C}}-\text{CO}-\text{CH}_3$.

If this condensation is carried out in the presence of alkali, the reaction product does not react with bleaching powder.

EXPERIMENTAL

We carried out the condensation of methyl ethyl ketone with benzaldehyde as follows: 25 g of methyl ethyl ketone and 25 g of benzaldehyde were introduced into a flask with a ground stopper, the mixture was cooled to 0°C and saturated with hydrogen chloride (during this operation the temperature rose 5 - 6°). After this the flask was closed and left to stand at room temperature for 2 days. The oily product formed was shaken with dilute alkali until the acid was completely removed. It was then washed several times with water and extracted with ether. The ethereal solution was dried with anhydrous sodium sulfate, freshly dried, and after removal of the ether the residue was distilled in vacuum. The distillate crystallized in large needles, melting at 39-40°.

The product so obtained was treated with chloride of lime. 50 g of the latter, containing 25% of available chlorine, was stirred up well in a porcelain basin with 120 ml of water. The mass obtained was transferred to a Wurtz flask, to which 6 g of the finely ground condensation product was added and the stopper of the flask replaced: this stopper carried a stirrer with a mercury seal. The lead-off tube was connected to a Liebig condenser. After 15-20 minutes mixing, the contents of the flask were observed to heat up. After the cessation of spontaneous heating, the flask was heated (for about 1 hour) on a water bath in order to complete the reaction, during which period chloroform slowly distilled off. As soon as the liberation of the latter ceased, the heating was discontinued. The residue in the flask was filtered through a Buchner funnel, the filtrate was acidified with dilute HCl, throwing down a white precipitate. The latter was separated from the mother liquor and washed with water. The mother liquor was well mixed in the flask with the material on the Buchner funnel and was heated for some time. This operation was repeated 2 - 3 times, until no further white precipitate was obtained on acidifying the filtrate.

The precipitate separated (2.9 g) was recrystallized from a mixture of water with a small quantity of alcohol, after being filtered through activated carbon.

The analytic data, indicating that the substance obtained was α -methyl-cinnamic acid, were: m.p. 77-78°, mol.wt. 163.5, mol.wt. for $C_{10}H_{10}O_2$ = 162.

The analysis of the silver salt also confirmed this:

0.3116 g substance: Ag 0.1229 g. Found%: Ag 39.44. $C_{10}H_9O_2Ag$. Calculated %: Ag 40.12.

The condensation of methyl ethyl ketone with benzaldehyde in alkali was performed as follows: 10.5 g of benzaldehyde (freshly distilled in CO_2) and 30.3 g of methyl ethyl ketone were mixed in a flask with 900 ml of water. The contents of the flask were stirred with a mechanical stirrer in order to form an emulsion. To this emulsion 10 g of 10% NaOH was added gradually and the stirring was carried on for three days. The contents of the flask were then neutralized with dilute sulfuric acid and the condensation product was extracted with ether. After drying the ethereal extract with freshly dried calcium chloride, the ether was distilled off, and the residue distilled under vacuum.

The condensation product thus obtained was treated with chloride of lime. No reaction was observed: there was no self heating nor liberation of chloroform, and the latter was not formed when the mixture was heated to 70-80° for one hour.

SUMMARY

1. The condensation of methyl ethyl ketone with benzaldehyde in the presence of acid occurs through the methylene group.
2. The condensation of methyl ethyl ketone with benzaldehyde in alkali occurs through the methyl group.

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PREPARATION OF WOOD CELLULOSE BY THE USE OF ORGANIC SOLVENTS

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The main aim of those who have investigated the cooking of wood with organic solvents has been the extraction of lignin. The most common organic reagents for separating lignin from wood are monohydric aliphatic alcohols, dioxane, etc. Frequently HCl and iodine are added as catalysts[1].

Wood is usually cooked as sawdust. In order to investigate lignin Nikitin extracted it from spruce with dioxane [2], and from larch with ethylene oxide [3]; Chudakov [4] extracted natural lignin by the destructive decomposition of wood with methanol.

Other investigations, very few in number, have been directed towards the study of the cellulose produced by this method.

An investigation has been reported [5], in which aspen sawdust was cooked with aqueous solutions or emulsions of alcohols and other organic reagents.

The opinion has been expressed [6] that, in the cooking of wood with organic solvents, part of the solvent combines with the lignin in the form of alkoxyl groups and thus brings it into solution [6].

The indicated method of cooking wood with organic solvents is of interest for two reasons: firstly, because it presents the possibility of obtaining cellulose, apparently of improved quality (as a result of the milder conditions of cooking), and secondly, because it makes it possible to extract from the wood the lignin relatively little changed, which is extremely important for the further study of its structure.

Bearing these considerations in mind, and also the fact that we have scarcely carried out any such work, we thought it useful to undertake this investigation.

EXPERIMENTAL

The investigation was commenced with an analysis of samples of four kinds, of wood - birch, aspen, spruce and fir. The results of the analysis are given in Table 1. Later these samples were used for cooking.

Cooking of sawdust. Birch and aspen sawdusts were used for cooking. In one series of experiments ethylene glycol-water was used as a cooking agent, and in another series, ethyl glycol-water (Experiments Nos. 1 - 6, Table 2). The conditions of cooking are indicated in Table 2. The quantity of lignin, pentosans, total cellulose and cellulose was determined in the mass after cooking, and also the hardness, by Beckmann's method, and the quantity of substance, extractible by a mixture of alcohol-benzene. The data are presented in Table 3.

Assuming that the fiber was contaminated by the products of organic breakdown and that we thus determined an enhanced lignin content, the mass was extracted with alcohol/benzene. After this a lignin content close to the true one was obtained (Table 3).

¹) Lab. workers E.I.Evtopena and B.M.Avrulina took part in the experimental part of this work.

Since the cooking of larch wood with an aqueous solution of ethyl glycol gave positive results, spruce and fir were treated with these reagents under similar conditions (Table 2, Experiments Nos. 7 - 8). The experiments were not successful. Attempts were made to cook fir sawdust, previously deresinated with ether and an alcohol/benzene mixture, using a mixture of butanol and water as a cooking agent. The results were again negative.

Cooking of shavings. The samples used were prepared from aspen and birch shavings (2 x 1.5 x 0.3 cm) and were cooked with an aqueous solution of ethyl glycol (Table 4, Experiments Nos. 10 - 13), using butanol/water mixture (Experiments Nos 14 - 15), and amyl alcohol/water (Experiments Nos. 18 - 19)¹. The cooking conditions are set out in the table, and the analysis of the mass in Table 5. The mass obtained was of different shades of dark yellow.

Fir shavings were also cooked with the butanol/water mixture (Table 4). The shavings were not cooked through. The content of lignin after the boil was 28.57%. Previously deresinated fir shavings were thrice cooked in fresh portions of the same cooking agent (Table 4). The results were negative. The lignin content of the shavings after cooking was 23.11%. With a small decrease in the lignin content there was observed a considerable fission of the carbon part of the wood (see Fig.). In the majority of the experiments the cooking was performed in an autoclave, of capacity 2.5 liters, electrically heated. 100 g of air dry shavings were charged in, and for hardwoods, 1 liter of solvent. In experiments with soft woods, and with amyl alcohol, in view of its lower cooking action, the quantity of solvent was increased. Smaller quantities of sawdust were used, 70-100 g; 1 - 1.5 liter of solvent was introduced. The time of cooking for hardwoods was 4 hours, and the temperature 155 - 180°.

After cooking the mass the sawdust was separated from the liquor by straining through a linen bag, and washed with water on a Buchner funnel; when shavings were being treated they were washed and sorted in situ. The fibers were yellowish to brown.

For analysis of bleached and unbleached cellulose from wood, the same methods were used.

The lignin content was estimated by the TsKAL method², in the determination of the pentosans the furfural content in the distillate was determined volumetrically (bromine method [7]). The cellulose content was determined by treatment of the fibers or sawdust with a mixture of alcohol and nitric acid [7]. α -Cellulose was determined by the standard method, by treating the fibers with 17.5% NaOH.

Bleaching, analysis and mechanical treatment of the bleached mass. Since cooking with organic reagents produced a yellow mass, experiments on the bleaching of the mass obtained from birch and aspen shavings (Table 6, Experiments Nos. 11, 13b 14, 15, 18 and 19) and the mass from fir shavings were undertaken (Experiment No.17).

¹) Experiments with amyl alcohol were executed by E.V. Allekseeva and N.A. Sitnikova, students of the technological faculty of the Leningrad Tech. Inst.

²) Central Analytical Control Laboratory.

TABLE 4

Analysis of Wood

Nature of wood	Moisture	Ash content	Ether solubles	Total cellulose	Lignin	Pentosans
Aspen	6.25	0.53	3.2	50.7	22.42	24.3
	6.37	0.64	3.01	51.3	22.45	24.5
	-	-	-	49.9	-	-
	-	-	-	49.6	-	-
Birch	6.31 ¹⁾	0.58	3.1	50.75	22.43	24.4
	6.54	0.3	1.48	50.87	18.5	24.18
	6.7	0.28	1.52	49.57	18.7	24.65
	-	-	-	48.27	-	-
Spruce	-	-	-	48.47	-	-
	6.61	0.29	1.50	49.3	18.6	24.41
	0.64	0.604	1.16	53.06	29.17	8.45
	0.58	0.704	1.00	52.38	29.19	7.8
Fir	0.61	0.654	1.08	52.72	29.18	8.1
	0.76	0.586	7.57	41.0 41.7	36.6	11.1
	0.64	0.606	7.5	41.3 41.2	36.4	12.2
	-	-	-	-	35.5	-
	0.7	0.596	7.53	41.4	36.2	11.65

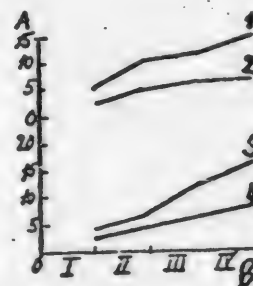
¹⁾ Here and in the following tables averaged values are given below the bracketed figures.

The bleaching was carried out with solution of bleaching powder at 37°, the available chlorine content of the solution being 28.2 - 44.6 g/liter. After bleaching the solution was made acid with sulfuric acid. The bleached mass was white, except for that from Experiment No.17, which remained light yellow. In Experiments Nos. 11, 13 and 14, the bleaching was performed in one stage, while in Experiments Nos. 15, 18 and 19 it was done in two stages, and in Experiment 17, in three.

After bleaching the mass was washed with water and soured with sulfurous acid. The concentration of the mass during souring was 5%, time 30 minutes.

The consumption of SO₂ was 5% on the weight of the fibers.

Grinding and mechanical investigation.
The grinding was performed in a ball mill. 26 g of fibers (calculated on the dry weight)



Delignifying action of organic solvents.

A - lignin (in %); 1 - after cooking (fir shavings); 2 - after extraction (fir shavings); 3 - after cooking (birch shavings); 4 - after extraction (birch shavings); B - solvents: I - ethylglycol; II - butanol; III - pentanol; IV - ethylene glycol.

TABLE 2

Results of Experiments on Cooking of Sawdust

Expt. No.	Wood	Weight of air-dry sawdust (in g)	Cooking agent		Conditions of cooking		Temperature	Pressure (atm.)	Yield of (cellulose) mass	
			Name	Quantity (in ml)	Duration				(in g)	(in %)
					Boiling (in hrs)	Cooking (in hrs)				
1	Birch (fine dust)	100	ethylene glycol/water	750	1.5	4	180	8	53.0	56.6
2	Birch (coarse dust)	70		750	2.7	4	176-180	-	35.0	54
3	Aspen (fine dust)	100		500	1.5	4	180	8	55.7	57.63
4	Aspen (coarse dust)	70		750	2.7	4	176-180	-	38.2	57.03
5	Birch (coarse dust)	80	ethyl glycol/water	500	2.7	2.0	176-180	-	31.0	41.8
6	Aspen (coarse dust)	80		500	2.7	4	176-180	-	32.5	42.4
7	Spruce (coarse dust)	80		500	2	4	150-160	9	39.8	51.1
8	Fir (coarse dust)	80		500	2	4	170	-	38.94	48.9
9	Fir (coarse dust) ¹⁾	80	butanol/water	500	0.66	4	160-163	8.5	41.0	57.36
				500						

1) The dusts were extracted before cooking with ether and benzene/alcohol mixture.

were ground at 60° for 4 hours. During the grinding samples were periodically withdrawn in order to determine their degree of subdivision in a Shopper-Rigler apparatus. Pressings of 4 - 4.2 g weight were made in a leaf pressing apparatus.

Mechanical investigations were made with strips of standard dimensions with a width of 1 cm. The tearing length, the number of double foldings, and the absorptive capacity were determined by the usual methods.

The pressings obtained had a considerable mechanical strength with the exception of those in Experiments Nos. 11 and 19. This can be explained by the fact that the method of cooking used for aspen wood was extremely severe. Experiments should be repeated under milder conditions. The experimental data are set out in Table 6.

Liquors. In experiments with ethyl glycol and ethylene glycol the liquors were homogeneous solutions having a brown color from which a precipitate came down on standing.

In experiments with butyl and amyl alcohols the liquors separated. The upper layers were dark brown and alcoholic; the lower layers were light red and aqueous.

The liquors were not investigated or regenerated.

TABLE 3

Analysis of mass from dust

Expt. No.	Substances extractible with alcohol/benzene mixture (%)	Hardness (Berkman)		Lignin		Total cellulose		Cellulose		Pentosans	
		Before extraction	After extraction	Before extraction	After extraction	Before extraction	After extraction	Before extraction	After extraction	Before extraction	After extraction
1	-	133.7	93.56	16.95	8.13	77.6	84.1	74.2	-	14.0	14.68
		130.0	-	16.47	8.3	77.7	84.9	75.7	-	13.97	13.96
		-	-	16.6	-	-	-	-	-	15.0	-
		-	-	16.0	-	-	-	-	-	15.1	-
		-	-	15.9	-	-	-	-	-	13.96	-
2	7.39	131.85	-	16.35	8.22	77.65	84.5	74.95	-	14.41	14.32
		124.75	-	-	5.93	-	87.28	-	84.7	-	13.0
		127.35	97.22	-	6.4	-	88.4	-	84.6	-	13.7
		128.75	-	-	-	-	-	-	-	-	-
		130.05	-	-	-	-	-	-	-	-	-
3	-	127.7	-	-	6.17	-	87.84	-	84.65	-	13.35
		85.95	-	13.95	7.64	79.2	86.9	79.99	-	10.0	12.2
		84.2	-	14.25	7.29	79.6	86.8	79.88	-	10.4	13.0
		-	-	-	-	-	-	-	-	-	13.3
		-	-	-	-	-	-	-	-	-	13.2
4	9.9	85.07	-	14.10	7.465	79.4	86.85	79.73	-	10.2	13.17
		129.35	65.5	-	5.70	-	87.5	-	84.2	-	10.9
		119.5	66.25	-	5.61	-	87.4	-	84.2	-	11.0
		134.25	-	-	-	-	-	-	-	-	-
		127.7	65.87	-	5.65	-	87.45	-	84.2	-	10.95
5	2.46	38.4	21.12	-	1.61	-	94.86	-	76.0	-	9.36
		-	-	-	1.51	-	94.3	-	-	-	9.37
		-	-	-	-	-	-	-	-	-	10.0
		-	-	-	-	-	-	-	-	-	11.0
		-	-	-	-	-	-	-	-	-	10.5
6	2.9	-	-	-	-	-	-	-	-	-	10.4
		48.5	15.85	-	1.56	-	94.58	-	-	-	10.24
		48.8	15.85	-	1.29	-	95.5	-	-	-	1.2
		-	-	-	1.20	-	95.5	-	-	-	1.3
		-	-	-	-	-	-	-	-	-	2.4
7	4.2	-	-	-	-	-	-	-	-	-	1.9
		48.65	15.85	-	1.24	-	95.5	-	-	-	1.27
		64.68	-	-	18.9	-	83.5	-	-	-	2.1
		-	-	-	19.2	-	85.1	-	-	-	3.2
		-	-	-	-	-	-	-	-	-	-
8	10.0	-	-	-	19.05	-	84.3	-	-	-	2.65
		83.27	70.64	-	-	-	-	-	-	-	5.2
		-	69.96	-	28.0	-	71.94	-	-	-	4.7
		-	-	-	-	-	-	-	-	-	-
		-	-	-	-	-	-	-	-	-	-
9	1.2	64.1	70.30	-	-	-	-	-	-	-	4.95
		-	60.76	-	25.95	-	69.12	-	-	-	7.0
		-	-	-	26.05	-	68.55	-	-	-	7.6
		-	-	-	-	-	-	-	-	-	-
		-	-	-	26.0	-	68.83	-	-	-	7.3

TABLE 4
Cooking of shavings

Expt. No.	Wood	Air-dry weight of shavings (in g)	Cooking agent		Conditions of cooking				Yield	
			Name	Quantity (in ml)	Time		Temperature	Pressure (in atm)	(in g)	(in %)
					Boiling (in hours)	Cooking (in hours)				
10	Aspen shavings	100	Ethyl-glycol/water	500	0.83	4	160-165	8.5-9	27.0	37.0
11	Aspen shavings	100		500	0.7	4	155-160	7-7.5	43.1	46.88
12	Birch shavings	100		500	0.75	4	165-170	9	23.1	32.0
13	Birch shavings	100		500	0.66	4	145-150	4.3 ¹ 4.5 ²	29.6 22.0	32.78 24.28
14	Birch shavings	100	-	-	-	-	-	Total	57.06	
15	Aspen shavings	100	Butenol water	500	0.56	4	160-162	7.8-8	41.5	45.6
16	Fir shavings	100		500	1.5	4	160-164	8-8.5	48.5	52.23
17	Fir shavings	100		700	1.8	9	164-165	9	-	-
17a	Fir shavings	100		750	1.7	6	165-168	9-9.2	-	-
17b	Fir shavings	100		750	1.6	6	164-168	9-9.2	-	-
				500	1.6	6	164-168	9-9.2	25.6	27.95
		Total	2000	4.9	18	-	-	-	-
18	Birch shavings	100	Amyl alcohol/water	750	1.5	6	167-169	9-9.2	43.1	46.6
				750	1.5	2	169	9-9.2	-	-
19	Aspen shavings	100	Amyl alcohol/water	1000	1.5	4	167-169	9-9.2	-	-
				1000	1.5	2				
				1000	1.5	1	167-169	9-9.2	52.1	55.6

1) Slightly undercooked fiber.

2) Completely cooked fiber.

TABLE 5
Analysis of Unbleached Mass from Shavings

Expt. No.	Amount soluble in alcohol/benzene mixture, %	Hardness (Berkman)		Lignin (in %)		Pentosans (in %)		Total cellulose (in %)	
		Before extraction	After extraction	Before extraction	After extraction	Before extraction	After extraction	Before extraction	After extraction
10	4.3	-	35.3	-	2.65	-	2.7	-	95.1
	-	-	-	-	2.73	-	2.7	-	94.8
11	-	-	-	-	2.69	-	2.7	-	94.95
	-	78.8	-	-	2.03	-	5.8	-	93.58
	-	-	-	-	2.24	-	5.8	-	93.87
12	-	-	-	-	2.13	-	5.8	-	93.72
	4.0	-	38.56	-	2.28	-	5.75	-	94.81
	-	-	-	-	2.28	-	5.65	-	95.0
13a	-	-	-	-	2.28	-	5.70	-	94.90
	7.0	65.44	-	-	5.32	-	13.0	-	85.58
	-	-	-	-	5.06	-	12.9	-	85.6
14	-	-	-	-	5.19	-	12.95	-	85.59
	1.05	108.2	-	7.15	4.18	13.82	13.93	91.32	91.84
	-	107.9	-	-	4.14	13.44	14.0	-	91.73
15	-	108	-	-	4.16	13.63	13.96	-	91.84
	-	79.13	-	9.98	-	10.75	-	84.53	-
	-	-	-	9.9	-	10.62	-	84.11	-
18	-	-	-	9.94	-	10.68	-	84.32	-
19	-	108.8	-	12.62	-	10.57	-	-	-
	-	83.5	-	11.04	-	10.49	-	-	-

SUMMARY

1. Cooking of sawdust from hard woods (aspen and birch) with ethylene glycol gave a yield of 54-57.63% of mass, and with ethyl glycol a yield of 41.8-42.4%.

2. Cooking of shavings from soft woods with ethyl glycol gave a yield of 32-57.06%, with butanol 45.6-52.5%, with amyl alcohol 46.6-55.6%.

Removal of lignin from fir shavings with butyl alcohol was difficult and was accompanied by a considerable decomposition of the carbon part of the wood. Yield 27.9%.

3. Bleaching with solutions of bleaching powder improved the quality of the masses obtained.

4. The mechanical strength of the fibers obtained, in the majority of cases was good.

5. All the solvents indicated can be used for delignification of hard

TABLE 6
Leaching and Analysis of the Bleached Mass

Expt No.	Wood	Cooking agent	Quantity taken for bleaching	Concentration of bleaching solution (%)	Quantity of bleaching solution (g/L)	Time of bleaching	Source of SO ₂ in the mass (%)	Time of cooking (min)	Lignin (%)	Mass after cooking (%)	Moisture content (%)	Degrees of grinding	Penetration of liquor	No. of double screenings	Investment	
11	Aspen (shavings)		38.65	10	84.2	44.65	3hr 40m	5	30	0.62	6.7	93.6	-	-	1673.3	2.5
				-	-	-	-	-	-	0.57	6.1	93.4	-	-	1384.8	2.6
				-	-	-	-	-	-	-	-	-	-	-	1615.6	2.5
13b	Birch (shavings)	Ethyl glycol water	15.3	18	67.4	41.9	3hr 40m	5	30	0.6	12.07	90.40	81.32	-	6361	2554.22
				-	-	-	-	-	-	0.6	11.87	90.36	-	-	6411	1305.22
				-	-	-	-	-	-	-	-	-	-	-	5188	-
14	Birch (shavings)	water	33.8	18	139.7	43.5	3hr	5	30	0.6	11.97	90.38	-	-	5985	1429.22
				-	-	-	-	-	-	0.42	12.22	93.58	82.52	60	5611	1663.19
				-	-	-	-	-	-	0.42	12.14	93.54	83.1	-	5833	1829.20
				-	-	-	-	-	-	-	-	-	-	-	6093	-
15	Aspen (shavings)	Ethanol water	40.8	15	142.7	42.8	4hr 20m	5	30	0.72	11.28	93.94	82.47	59	4727	1681.27
				-	-	-	-	-	-	0.70	11.35	94.1	82.33	-	4990	1182.27
				-	-	-	-	-	-	-	-	-	-	-	5947	-
				-	-	-	-	-	-	-	-	-	-	-	5282	-
17	(shavings)	Ethanol water	14	195	152.7	-	-	-	-	0.71	11.31	94.02	82.4	-	5236	1139.27
				10	-	-	15m	5	30	2.24	4.57	-	-	-	-	-
				5	-	-	-	-	-	2.78	4.6	-	-	-	-	-
				3	-	-	-	-	-	-	-	-	-	-	-	-
18	Birch (shavings)	Amyl alcohol water	35.0	13	155.3	29.53	40m	5	30	0.93	10.32	93.15	-	-	4125	74.23
				9	106.5	29.53	2hr 05m	-	-	0.95	10.35	93.19	-	-	4191	72.23
				22	261.8	-	2hr 45m	-	-	0.94	10.33	93.17	86.0	-	4158	73.23
19	Aspen (shavings)		37.5	11.5	147.1	29.53	50m	5	30	0.72	10.22	94.26	-	-	1559	0.27
				9.0	114.4	29.53	2hr 20m	-	-	0.70	10.30	94.38	-	-	1639	0.27
				20.5	261.5	-	3.10	-	-	0.71	10.26	94.31	83.97	-	1589	0.27

woods. The best results were obtained with ethyl glycol.

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